



COORDINATION CHEMISTRY OF ELECTRON RICH NITROGEN/PHOSPHORUS CONTAINING ORGANIC MOIETIES WITH TRANSITION METALS

ABSTRACT

Ph. D. THESIS

BY



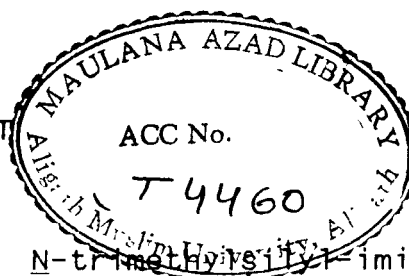
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1991

ABSTRACT



Reactions of the reagents N-trimethylsilyl-imidazole ($\text{Me}_3\text{Si-Iz}$) and N-trimethylsilyl-2-methylimidazole ($\text{Me}_3\text{Si-MeIz}$) towards M-Cl bonds in transition metal chlorides and their derivative complexes with π -bonding ligands as well as in a few organometallic derivatives have been investigated and discussed in this work. The reagents have been obtained by refluxing the appropriate heterocycle i.e. imidazole or 2-methylimidazole with N,N bis(trimethylsilyl)amine (commonly known as hexamethyldisilazane) in the presence of little amount of conc. H_2SO_4 in an inert atmosphere of N_2 followed by fractional distillation. As the reagents are moisture sensitive, the reactions with metallic substrates have been performed in strictly anhydrous conditions.

Both, $\text{Me}_3\text{Si-Iz}$ as well as $\text{Me}_3\text{Si-MeIz}$ showed considerable reactivity towards the metal chlorides and the corresponding complexes. The observed reactivity may be attributed to the affinity of $(\text{CH}_3)_3\text{Si-}$ group in the reagent for chlorine atom in the substrate effecting the release of $(\text{CH}_3)_3\text{SiCl}$.

Reactions of $\text{Me}_3\text{Si-Iz}$ or $\text{Me}_3\text{Si-MeIz}$ with anhydrous CoCl_2 has afforded the final product as $[\text{CoLCl}]$ (I) or (II) (L =imidazolate or 2-methylimidazolate), where only one

(ii)

chlorine atom has been substituted with the heterocyclic moiety, even though, a slight excess of the reagents from that required for the total replacement of chlorine atoms were used. Interestingly, in the analogous reactions with $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$, replacement of both the chlorine atoms alongwith total release of free Ph_3P (a strong π -acid) from the substrate yielding $[\text{CoL}_2]$ (III), (IV) has been observed. The stoichiometry of the complexes and the mode of bonding with probable molecular formulations have been ascertained using various physico-chemical methods.

Reactions of RuCl_3 and a few of Ru (II) and Ru(III) complexes with π -acids possessing Ru-Cl bond(s) have also been investigated. The products of these reactions are invariably oligomeric in nature involving imidazolate bridging to generate an octahedral environment around Ru(II) or Ru(III) ion as evidenced from magnetic moment and electronic spectral studies. The latter suggests that the ligand to metal charge-transfer excitation is stabilized (lower in energy) due to π -donor nature of the imidazolate moiety and there is possibility of mixing between d orbital on Ru(III) and the π -system of ligand.

Reactions of $\text{Me}_3\text{Si-Iz}$ and $\text{Me}_3\text{Si-MeIz}$ with CuCl_2 and $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$ have afforded $[\text{CuL}_2]$ (V), (VI) and $[\text{Cu}(\text{Ph}_3\text{P})_2\text{L}]$ (VII), (VIII). The results of the physico-chemical studies are in agreement with square-planar and a tetrahedral

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arrangement of ligands around Cu(II) and Cu(I) ion respectively.

It is noteworthy, that reaction of NiCl_2 with $\text{Me}_3\text{Si-Iz}$ or $\text{Me}_3\text{Si-MeIz}$ has proceeded with complete substitution of the chlorines yielding $[\text{NiL}_2]$ (XVII), (XVIII) while with PdCl_2 or its derivative complexes, the molecular unit of the final product has always retained a chlorine atom. The infra-red spectral informations suggest that in Pd(II) derivatives, the probable dimerization occurs through the imidazolate bridging resulting in a square-planar geometry of the complexes, which has been confirmed from the observed diamagnetic nature of the complexes as well as their electronic spectral studies. The reactions of $[\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ proceeded with the liberation of two moles equivalent of Ph_3P affording $[\text{NiL}_2]$ (XVII), (XVIII), however with $[\eta^5\text{-C}_5\text{H}_5)(\text{Ph}_3\text{P})\text{NiI}]$ the final product is $[(\eta^5\text{-C}_5\text{H}_5)(\text{Ph}_3\text{P})\text{NiI}]$ (XIX), (XX). The analytical data are in good agreement with the proposed stoichiometry of the complexes. The magnetic moment data, and the spectral studies including i.r., $^1\text{Hn.m.r.}$, $^{31}\text{Pn.m.r.}$ and U.V.-visible spectra, suggest tetrahedral structure of (XIX) and (XX). The electronic (Ligand field) spectrum of $[\text{NiL}_2]$ (XVII), (XVIII) is compatible with a square-planar geometry, however, the complexes possess some paramagnetism (μ_{eff} Ca. 1.0 B.M.), rather, as expected, to be diamagnetic in nature. This

observed anomalous μ_{eff} value suggests that the ground electronic state of Ni (II) in $[\text{NiL}_2]$ is near the magnetic cross-over point concomitant with the singlet-triplet spin state equilibrium.

It has been observed that reactions of $[\text{M}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ ($\text{M} = \text{Ni}, \text{Pd}$ or Pt) with the reagents proceed with the liberation of two, one and none mole equivalent of free Ph_3P in the order Ni, Pd and Pt respectively. This has been correlated to the inherent nature of the individual precursor vis-a-vis to the π -acceptor tendency of Ph_3P , which is known to be more pronounced in $\text{Pt}(\text{II})$ complexes where an enhanced labilization (i.e. trans-effect) of ligand is usually observed.

It has been found that $\text{Me}_3\text{Si-Iz}$ or $\text{Me}_3\text{Si-MeIz}$ can be exploited as a potent reagent for the preparation of hitherto elusive, R_2SnL_2 ($\text{L} = \text{imidazolate}$ or $2\text{-methylimidazolate}$) (XXVII), (XXVIII), (XXIX), (XXX) utilizing the metathetic exchange with the corresponding R_2SnCl_2 . However, the previously known methods like condensation reaction of R_2SnO or 1,3 cycloaddition reaction have invariably produced trialkyl or triaryl - derivatives i.e. R_3SnL . The analytical data confirm the stoichiometry of the product(s) and i.r. and ^1H n.m.r. spectral data indicate that R_2SnL_2 adopts octahedral geometry involving intermolecular imidazolate

bridging. Reaction with SnCl_2 has produced $[\text{SnClL}]_2$ (XXXIII) (XXXIV), even though, an excess of the reagent was used to cause complete replacement of the chlorines as $(\text{CH}_3)\text{SiCl}$. The physico-chemical data suggest that the dimer $[\text{SnClL}]_2$ involves imidazolate bridging which however, could not be transformed into a monomeric species, even if reacted with strong bases like pyridine, pyridine N-oxide (PyNO), bipyridine and $^n\text{Bu}_4\text{N.I.}$ The adduct $\text{SnCl}_2.\text{pyNO}$ has also produced $[\text{SnClL}]_2$ with liberation of free PyNO in the reaction mixture when reacted with the reagent. This behaviour of the dimer can be rationalized in terms of the presence of strong bridging capability provided by the imine (pyridyl) nitrogen of the imidazolate moiety resulting in an intact dimer.

Reaction of (XXXIII) or (XXXIV) with excess Ph_3P under refluxing condition has afforded the adduct $[\text{SnL}_2 (\text{C}_6\text{H}_5)_3\text{P}]$ (XXXV), (XXXVI) which undergo oxidative addition reaction with iodine producing $[\text{SnL}_2\text{I}_2]$ (XXXVII), (XXXVIII) with complete liberation of Ph_3P . All these products have been characterized from analytical data, i.r., ^1H n.m.r., and ^{31}P n.m.r. spectroscopic studies. The precursors $[\text{M} (\text{Ph}_3\text{P})_2\text{Cl}_2]$ ($\text{M}=\text{Zn}$, **Cd** or Hg) exhibit considerable reactivity towards the reagents giving quantitative yield of the product $[\text{Zn}(\text{Ph}_3\text{P})_2\text{L}_2]$ (XXXIX), (XL); $[\text{CdL}_2]$ (XLI), (XLII) and $[\text{Hg}(\text{Ph}_3\text{P})_2\text{L}_2]$ (XLIII), (XLIV). The stoichiometry and the

probable molecular formulations of these compounds have been ascertained from analytical and spectral studies.

The study of the ligating characteristic of an elusive P(III) derivative, $RP(NCS)_2$ ($R = CH_3, C_6H_5$) towards transition metal chlorides have been carried out and the results of the present studies are reported in this work. The ligands $RP(NCS)_2$ have been obtained utilizing the metathetic reactions of a thiocyanating agent $AgSCN$ with the corresponding substituted phosphines $RPCl_2$ using an inert atmosphere of dry N_2 in non-polar organic solvent. An attempt to isolate the ligand in neat form free from the solvent has provided a decomposed product which did not correspond the proposed stoichiometry $R P(NCS)_2$. However, it exhibited considerable reactivity (in-situ) towards the transition metal salts affording stable solid complexes with the stoichiometries as $[MLCl]Cl$ [where $L = CH_3P(NCS)_2, C_6H_5(PNCS)_2$; $M = Mn$ (XLV), (XLVI); Co (XLVII), (XLVIII); Ni (XLIX), (L); Cu (LI), (LII)]; $[MLClCl_2]$ [$M=Fe$ (LIII), (LIV); V (LV), (LVI)] and $[CuLCl]$ (LVII), (LVIII). These compounds have been characterized by elemental analyses, conductometric and magnetic susceptibility measurements and i.r., ^{31}P n.m.r. and electronic (ligand field) spectral studies. The present studies indicate that the $- P(NCS)_2$ moiety retains its identity in the complexes providing P and S chelating centres. ^{31}P n.m.r. data suggest that chelation to metal ions

is accompanied with delocalization of metal electrons through an additional overlap between empty p ($3d\pi$) and metal ($3d\pi$) orbitals. The complexes are monomeric, behaving as 1:1 electrolytes excepting for $[\text{CuLC1}]$ (LVII), (LVIII) (non-electrolyte) and $[\text{MLCl}]\text{Cl}_2$ (LI) - (LVI) (1:2 electrolytes) in DMSO. A tetrahedral configuration has been found for (XLVII), (XLVIII) while Ni (II) complexes (XLIX), (L) adopt square-planar structure. In the absence of magnetic and ligand field data for $[\text{CuLC1}]$ (LVII), (LVIII) due to d^{10} configuration of the metal ion, the tetrahedral geometry has been proposed in view of the conductance and analytical data of the complexes.



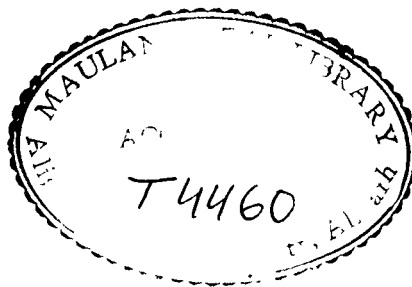
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**BY
SHAHBA NUSRAT QIDWAI**

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Certified that the work embodied in this thesis entitled, "Coordination Chemistry of Electron Rich Nitrogen/Phosphorus Containing Organic Moieties with Transition Metals" is the result of original researches carried out by Miss Shahla Nusrat Qidwai under my supervision and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh.

Zafar Ahmad Siddiqi

(Zafar Ahmad Siddiqi)

Reader in Inorganic Chemistry

DEDICATED

TO MY

Nana Abbu Janab Alhaj Mujeeb Ullah Sb.

AND

Mummy, Papa, Naaz and Faisal

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*"In the name of Allah
most Beneficial most Merciful"*

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Shahla Nusrat Qidwai
(SHAHLA NUSRAT QIDWAI)

LIST OF PUBLICATIONS

1. Reactions of N-trimethylsilyl-imidazole and -2-methyl-imidazole with anhydrous CoCl_2 and $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$; synthesis and physico-chemical studies on two-coordinate cobalt(II).
Trans. Met. Chem., 13, 244 (1988).
2. Reactivity of N-trimethylsilyl-imidazole and -2-methyl-imidazole; synthesis and physico-chemical studies on transition metal imidazoles and mixed ligand imidazoles.
Trans. Met. Chem., 13, 317 (1988).
3. Synthesis of bis(imidazolato)-dialkyltin(IV) and covalent tin(II) imidazolate derivatives.
J. Chem. Res.(S), 328 (1990).
4. Coordination complexes of labile phosphorus (III) derivatives $[\text{RP}(\text{NCS})_2]$ ($\text{R}=\text{CH}_3$, C_6H_5) with first row transition metals.
Bull. Soc. Chim. Fr., 127, 193 (1990).

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ABSTRACT

Reactions of the reagents N-trimethylsilyl-imidazole ($\text{Me}_3\text{Si-Iz}$) and N-trimethylsilyl-2-methylimidazole ($\text{Me}_3\text{Si-MeIz}$) towards M-Cl bonds in transition metal chlorides and their derivative complexes with π -bonding ligands as well as in a few organometallic derivatives have been investigated and discussed in this work. The reagents have been obtained by refluxing the appropriate heterocycle i.e. imidazole or 2-methylimidazole with N,N bis(trimethylsilyl)amine (commonly known as hexamethyldisilazane) in the presence of little amount of conc. H_2SO_4 in an inert atmosphere of N_2 followed by fractional distillation. As the reagents are moisture sensitive, the reactions with metallic substrates have been performed in strictly anhydrous conditions.

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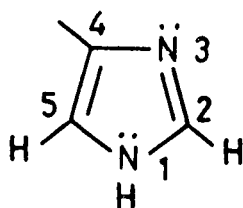
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is accompanied with delocalization of metal electrons through an additional overlap between empty p ($3d\pi$) and metal ($3d\pi$) orbitals. The complexes are monomeric, behaving as 1:1 electrolytes excepting for $[\text{CuLC1}]$ (LVII), (LVIII) (non-electrolyte) and $[\text{MLC1}]\text{Cl}_2$ (LIII) - (LVI) (1:2 electrolytes) in DMSO. A tetrahedral configuration has been found for (XLVII), (XLVIII) while Ni (II) complexes (XLIX), (L) adopt square-planar structure. In the absence of magnetic and ligand field data for $[\text{CuLC1}]$ (LVII), (LVIII) due to d^{10} configuration of the metal ion, the tetrahedral geometry has been proposed in view of the conductance and analytical data of the complexes.

The imidazole ring as a histidine moiety functions as ligands towards transition metal ions in an array of biologically important molecules including iron-porphyrin system, vitamin B₁₂ and its derivatives and several metalloproteins. It is believed that it is a histidine unit in the globin molecule which forms a bond with the heme molecule. This bond is between the imidazole nitrogen atom and the iron atom of heme. Free heme is insoluble in water and is readily oxidized by oxygen to the ferric compound, hematin. When heme is combined with globin, solubility in water is increased. The most important characteristic of the hemoglobin (ferrohemoglobin) is its ability to react reversibly with oxygen without changing the valency of iron. The addition of oxygen is referred to as oxygenation. Oxygen is taken up where its partial pressure is high as in lungs and given off at lower partial pressures in the tissues which are supplied with arterial blood. One mole of oxygen is taken up for each iron atom. It has been suggested that in hemoglobin itself there exists an ionic linkage between the imidazole nitrogen and the heme iron, but when oxygenation occurs there is a change to a covalent bond.¹ In the oxygenation step the oxygen molecule coordinates with the iron.

The structural features associated with the imidazole ring must be discussed briefly. The parent imidazole falls in the class of the aromatic heterocycles, and its unique structural features are conveniently discussed with reference to pyridine and pyrrole, to both of which imidazole is structurally related. Aromaticity in completely conjugated monocyclic systems require a planar array of atoms with $4n+2\pi$ electrons². The possibility for aromaticity in imidazole can then be recognized if imidazole is considered to be constructed from a trigonal nitrogen with two electrons in the unhybridized p orbital (N-1, "pyrrole nitrogen"), a trigonal nitrogen with a lone pair in a hybrid orbital and a single electron in the p orbital (N-3, "pyridine nitrogen") and three trigonal carbons each with one electron in a p-orbital. An Aromatic sextet is thus available (Figure-I).

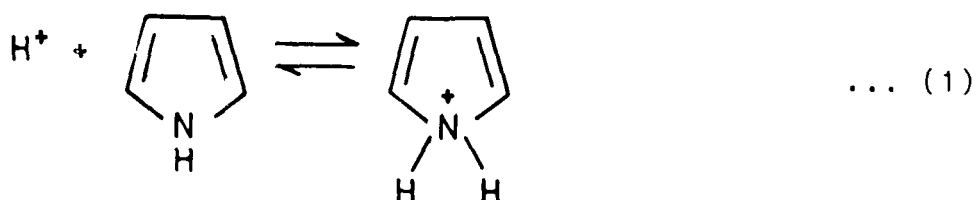


(Figure-I)

Imidazole is indeed generally regarded as being aromatic. The molecule is planar as anticipated for a molecular system³. In bonding⁴, the pyridine nitrogen displays functional negative σ and π electronic charges

indicating that this nitrogen is a modest σ -acceptor and a weak π -acceptor. The pyrrole nitrogen donates substantial fractional electronic charge to π -system but withdraws an even greater amount of charge from the σ orbitals so that the total result is a gain of the electronic charge at the pyrrole N-1 nitrogen of the imidazole.

A crucial structural feature with respect to the coordination site of imidazole is clarified when the aromatic nature of the molecule is recognized. There is only one pair of electrons properly described as an unshared pair, the pair on the N-3. The π electrons of N-1 are part of the aromatic sextet. Bonding of a proton or metal ion at N-1 is very unfavourable since the aromaticity of the ring is thereby compromised. The basicity at this type of site towards a proton can not be measured in pyrrole because protonation⁵ at carbon intervenes with a pK_a of -3.8. It has been estimated⁶ that the equilibrium constant for the reaction shown by equation (1) i.e.

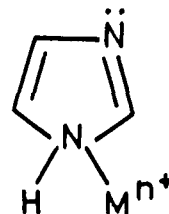


is 10^{-10} ($pK_a = -10$). The pyrrole nitrogen of imidazole should be of comparable, or probably lower basicity because

of the additional electron withdrawing effect of the pyridine nitrogen. The important conclusion is that the neutral imidazole molecule presents a single energetically favourable coordinating site for a proton. The unshared pair on N-3 and the same is most likely true for a metal ion. Structures shown in figure (II) and figure (III) must be of very high energy. The transfer of the N-1 proton to N-3 would be very favourable energetically and species shown in figure (II) and (III) would not be expected to be observable.



(Figure-II)

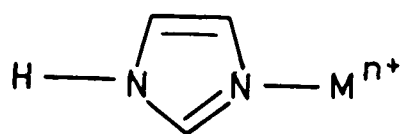


(Figure-III)

The structure of the protonated and metal ion complexes of imidazole are the aromatic cations (Figure-IV, V).



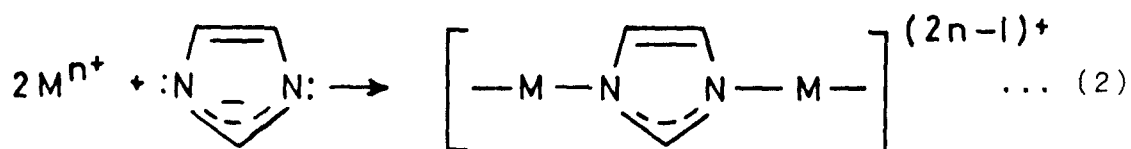
(Figure-IV)



(Figure-V)

Distinction between the N-1 and N-3 nitrogens is lost in the protonated imidazolium cation. Since this cation is

symmetrical, H-4 and H-5 are equivalent and a single peak appears in the proton magnetic resonance spectrum. A single averaged peak for the H-4 and H-5 protons also persists in the basic solutions of neutral imidazole because proton exchange reactions between N-1 and N-3 are rapid compared to the chemical shift difference between H-4 and H-5. In aqueous solutions tautomeric equilibration of the nitrogen bound hydrogen occurs without disruption of the aromatic electronic structure in proton exchange reactions with solvent species. In addition to protonation at N-3 with $pK_a = 7.1$ to give the imidazolium cation, neutral imidazole undergoes deprotonation⁷⁻⁹ at N-1 in strongly basic solutions [pK_a 14.2-14.6]. The resulting anionic imidazole also aromatic possesses two equivalent sites for coordination and is a potential bridging ligand (as shown below) although it is never a major component of the mixture in aqueous solution at equilibrium.



The ylide formed by the deprotonation of the imidazolium ion at C-2 can play a significant role in the chemistry of imidazoles. The exchange of the proton at C-2

A survey of literature reveals that 4,5-dimethylimidazole, 4-chloroimidazole, 4-aminomethyl and N-substituted 4-aminomethylimidazoles cause vaso-constriction and increase in blood pressure²². 1-Decyl-2-methylimidazole is said to be a typical anaesthetic²³. It has also been shown that 2-thio-4-aminomethylimidazole is said to possess some insulin like action in diabetes²⁴, 4,5(β -aminoethyl)imidazole stimulates smooth muscle²⁵ and exerts a profound effect on the mammalian circulatory system. It first causes a transient vaso-constriction, especially of the pulmonary vessels and then a general vaso-dilation occurs, accompanied by a fall in blood pressure²⁶. It is a strong gastric stimulant causing increased gastric secretion. It also increases the blood sugar content²⁷. Release of histamine or a histamine like substance is believed to be responsible for certain allergic manifestations in the human body, including bronchial asthma and urticarial eruptions²⁸. It therefore, appears that the extent and direction of physiological effects are largely controlled by the nature of substituents, present on the imidazole ring.

Dimethylbenzimidazole supplies one of the nitrogen atoms to be coordinated to Co(III) in vitamin B₁₂²⁹. The insulin hexamer is reported to have two zinc ions, each bonded to imidazole end of three histidine units³⁰. A variety of metal complexes of imidazolthiol are reported to exhibit

fungicidal and insecticidal behaviour, however, in some cases the antioxidant and heat resistant properties have also been noted³¹⁻³⁴. The possibility of the use of the imidazole complexes as anti-tumour drug has also been reported³⁵. Imidazole is also used as an analgesic, antipyretic and antiinflammatory reagent³⁶.

Imidazole and its derivatives are well known to yield coordination compounds with several metal ions³⁷⁻⁴². It may coordinate metals through lone pairs at either N-3 or N-1 or both. Though in majority of the cases coordination is reported via N-3 but there are several examples which favour N-1 coordination^{43,44}. Furthermore, the N-1 hydrogen possesses acidic character⁴⁵ ($pK_a=14$) and therefore imidazole or its derivatives can coordinate in the anionic form too. Examples are $Ag^+(C_3H_3N_2)^-$ and $Ni^{2+}(C_3H_3N_2)_2^-$. A variety of compounds containing uncharged imidazole (IzH) have been reported. The coordination compounds with this ligand can be divided into two classes.

- (a) Adducts of formula $[MX_n.(IzH)_m]$ with X^- coordinated to M.
- (b) Solvates of formula $[M(IzH)_m]^{n+}(X)_n^-$ with anions present only in the second coordination sphere of M^{n+} .

The adducts of the types (a) reported are : $[MCl_4(IzH)_2]$ ($M=Sn, Ti, Zr, Hf, Th$)⁴⁶⁻⁴⁷; $[MX_2(IzH)]$ (with $M=Mn, Ni, Cu$ and $X=Cl, Br, I$)^{38,39}; $[MX_2(IzH)_2]$ (with $M=Mn, Ni, Cu, Zn$ and $X=Cl, Br, I$)^{38,39,48}; $[MX_2(IzH)]$ (with $M=Co$ and Ni and

$X = \text{Cl}, \text{Br}, \text{I}$ ^{38,39} and with $M = \text{Mn}$ and $X = \text{Cl}$)³⁸; $[\text{M}(\text{NO}_3)_2(\text{IzH})_2]$ (with $M = \text{Co}, \text{Cu}$ and Zn)³⁸ $[\text{Mn}(\text{CNS})_2(\text{IzH})_2]$ ³⁸.

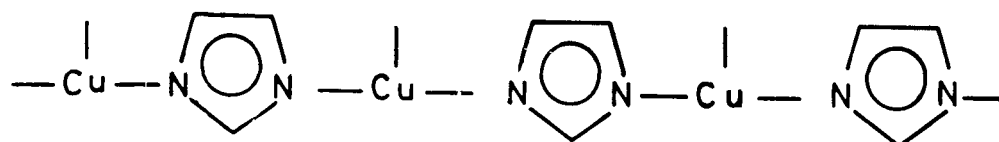
The solvates of the latter type i.e. (b) are also known but their numbers are comparatively small, they are: $[\text{M}(\text{IzH})_6\text{X}_2]$ (with $M = \text{Mn}, \text{Co}, \text{Ni}$ and $X = \text{Cl}, \text{Br}, \text{I}$)^{38,49}; $[\text{M}(\text{IzH})_6(\text{NO}_3)_2]$ (with $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$)^{38,49}; $[\text{M}(\text{IzH})_4(\text{NO}_3)_2]$ with $M = \text{Cu}, \text{Zn}$)^{38,49}; $[\text{Mn}(\text{IzH})_6(\text{CNS})_2]$ ³⁸; $[\text{Zn}(\text{IzH})_6\text{Cl}_2]$ ^{38,50} and $[\text{Ag}(\text{IzH})_2\text{NO}_3]$ ⁵¹.

In all these compounds the coordination site of the ligand was suggested to be the pyridine nitrogen (N-3) which has been later confirmed from single crystal X-ray structure determination on some of these complexes^{48,50}.

The coordination number of most of the metal ions in the adducts and solvates appeared to vary from tetrahedral e.g. in $[\text{CoCl}_2(\text{IzH})_2]$ ³⁹ to octahedral as in $[\text{Ni}(\text{IzH})_6(\text{NO}_3)_2]$ ⁴⁹ with square planar intermediates for the $\text{Cu}(\text{II})$ compounds.^{38,39} The methods used for the investigations were visible spectroscopy, infra-red spectroscopy and molecular weight, conductivity and magnetic moment data. The imidazole solvates of a series of tetrafluoroborates and perchlorates of divalent metals are also reported⁴².

In sufficiently basic media the conjugate base (Iz) of imidazole is formed which may also function as a ligand. With dipositive metal ions it has tendency to form compounds of

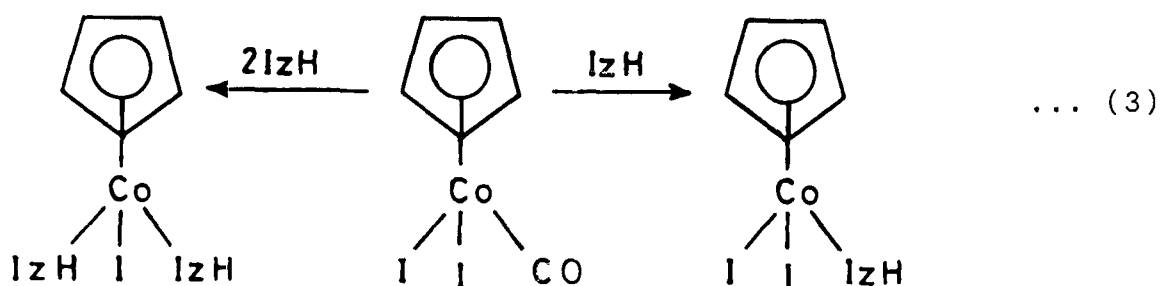
stoichiometry $[M(Iz)_2]$. These materials have usually been found insoluble and generally considered to be polymeric in nature. Examples reported are for the $Fe(II)^{52}$, $Cu(II)^{53,54}$, $Zn(II)^{53,54}$, $Co(II)^{49,54}$ and $Ni(II)^{49,53}$ systems. The coordination around $Zn(II)$ in $[Zn(Iz)_2]$ and $Co(II)$ in $[Co(Iz)_2]$ is tetrahedral⁴⁹. A distorted square planar arrangement has been observed⁵⁵ for $[Cu(Iz)_2]$ and postulated⁴⁹ for $[Ni(Iz)_2]$ ⁴⁹. Three different forms⁵⁶ of $[Cu(Iz)_2]$ have been described which differ in colour and also in magnetic behaviour, however their detailed structures are unknown. The imidazolate salt of $Cu(I)$ has also been reported⁵⁷, for which a polymeric bridge structure (Figure-X) has been proposed i.e.



(Figure-X)

Attempt has been made to draw some generalizations on the nature of imidazole bonding, based on the X-ray structural informations. Freeman and Szymanski¹⁵ noted that all complexes of neutral imidazole derivatives involved coordination through pyridine nitrogen. In complexes involving neutral monodentate imidazole ligands the metal ion is usually nearly co-planar with the imidazole ring. A large

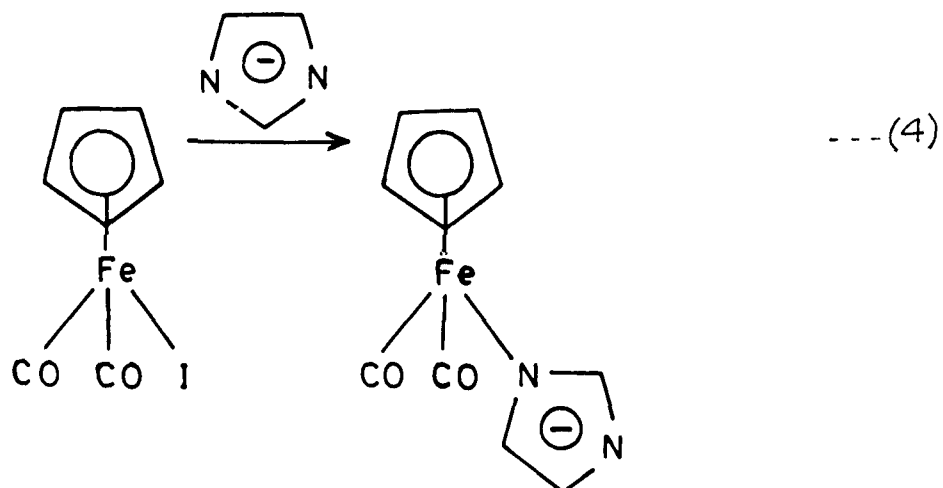
deviation was found in the $[\text{Co}(\text{2-MeIzH})_4(\text{NO}_3)_2 \cdot 0.5\text{EtOH}]$ ⁵⁸ structure where the cobalt is nearly 0.4°A out of coplanarity with one of the 2-methylimidazolate rings. Smaller deviations are reported in $[\text{Ag}(\text{IzH})_2(\text{NO}_3)]$ ^{59,60} and $[\text{Cu}(\text{IzH})_2\text{Cl}_2]$ ⁶¹. However, substantial deviations from co-planarity occur in cases where the ligand is in anionic form (i.e. Iz) as for example in $[\text{Cu}_3(\text{IzH})_8(\text{Iz})_2\text{ClO}_4]$ ⁶², $[\text{Cu}(\text{Iz})_2]$ ⁵⁵ and $[\text{Zn}(\text{Iz})_2]$ ⁵⁵. The bond distances in the complexed imidazole ring do not vary much from those in the free ligand⁶³. It has been observed that imidazole exhibits⁶⁴ a considerable nucleophilic activity towards transition metal carbonyl and iodide complexes i.e. it effects displacement of the CO and iodide from these complexes as for example shown below in the cyclopentadienyldiiodocobaltcarbonyl.



There is so far no report of complex in which the imidazole acts as a π -type ligand.

Attempts to make "diazoferrocenes", introducing imidazole as a π -bonded ligand have given the products in

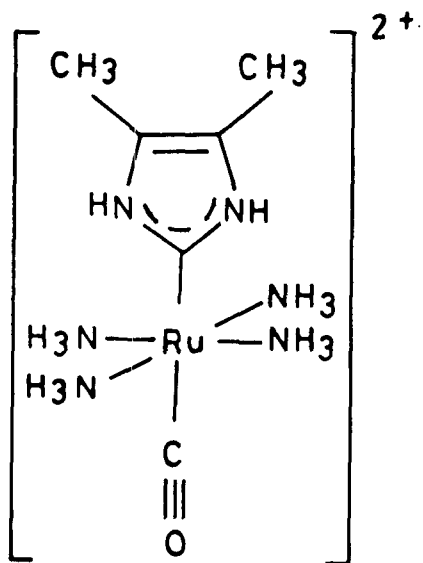
which the bonding is through pyridine lone pair⁶⁵. "Monoazaferrocenes" derived from imidazole are known but are reported^{66,67} to have limited stability.



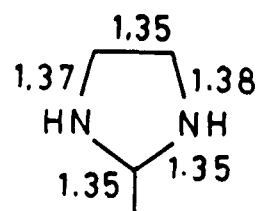
In exception to the behaviour of coordination through pyridine nitrogen i.e. N-3 and or pyrrolic nitrogen i.e. N-1 of imidazole there are certain complexes of ruthenium amines⁶⁸⁻⁷¹ in which the ligand is bound to ruthenium at carbon-2 of the ring. The ligand bound in this mode is formally the imidazolium ylide, a neutral dipolar tautomer of imidazole possessing an unshared pair of electrons (σ^-) on carbon-2. Sundberg et. al.^{68,69} were the first to prepare and characterize a number of C-bound imidazole complexes of ruthenium.

As has been mentioned above the imidazole ring can be bound to transition metal via the carbon-2. Imidazole and several of its C-4 and C-5 substituted derivatives^{68,69} form ions of composition $[(\text{NH}_3)_4\text{Ru}(\text{IzH}_2)\text{X}]^{+2}$ with Ru(II) and Ru(III) where X can be Cl^- , H_2O or CO. The carbon bound

arrangement suggested earlier from n.m.r. studies of the diamagnetic Ru(II) compounds was later confirmed⁶⁹ by a crystal structure determination on the hexafluorophosphate salt (Figure-XI) of the complex ion.



(Figure-XI)

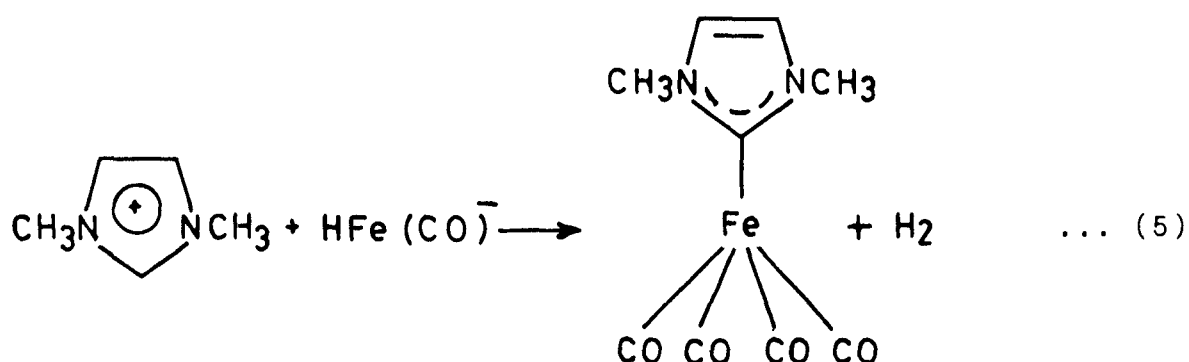


(Figure-XII)

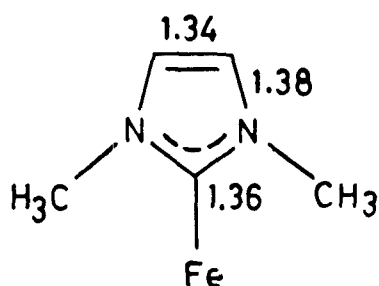
It has been observed that the bond lengths for the carbon bound ring (Figure-XII), indicate some shortening of the C-C bond relative to the N-coordinated ligand but remain in an aromatic range. The Ru(II) ion which is a very effective π -donor may be a particularly favourable case for this mode of bonding since in the C-bonded arrangement the imidazolium ion can act more effectively as a π -acceptor than the N-bonded structure. Ru(II) ion is in low spin state as is

Fe(II) in some of its complexes that occur in biological systems.

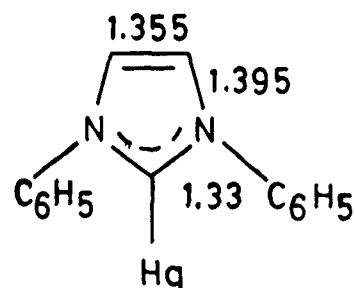
A similar type of carbon bonding has been found in $\text{Fe}(\text{O})$ ⁷², $\text{Cr}(\text{O})$ ⁷³ carbonyl compounds (as shown below in eq. (5) and in mercuric complex derived from the 1,3-diphenylimidazolium ion⁷⁴.



Crystallographic data for the $\text{Fe}(\text{O})$ ⁷⁵ (Figure-XIII) and $\text{Hg}(\text{II})$ ⁷⁶ (Figure-XIV) species suggest that the ring dimension in these ions are quite similar. The chemistry of these carbon bound complexes is still under exploratory stage at this time.

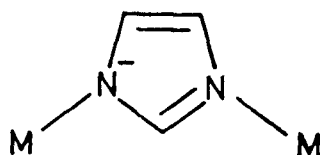


(Figure-XIII)



(Figure-XIV)

Diazoles (e.g. imidazole as shown in Figure-XV) and other nitrogen heterocycles having two or more nitrogen atoms in a molecule exhibit a potential capacity to coordinate as "exobidentate ligands" on two different metal ions to form M-L-M links⁷⁷. This kind of bridging is characteristic of these nitrogen heterocycles in contrast with common "endobidentate ligands" such as in 2,2'-bipyridine. The M-L-M links give rise to dimeric clusters, chain molecules and two or three dimensional network structures. All these structural types when involve purine and imidazole ligand are particularly interesting⁷⁷ in relation to electronic state of metal complexes as well as those of biological interest.



(Figure-XV)

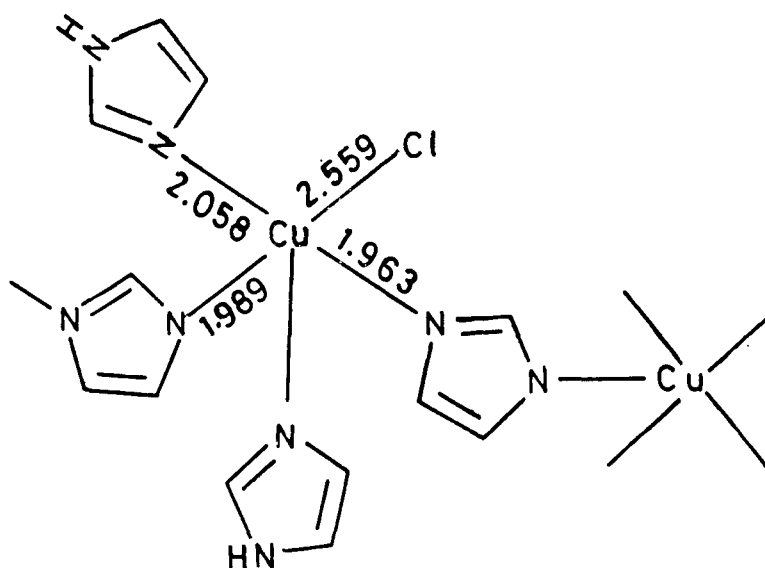
The coordination chemistry of bridged binuclear transition metal complexes has been the subject of extensive study^{78,79} in the recent past. Interest in this topic has been stimulated by the efforts of the bioinorganic chemists to synthesize model compounds for the coordination sites of metalloproteins⁸⁰. Particularly intriguing are hetero-

binuclear complexes⁸¹ where the influence of one transition metal on the physical and chemical properties of its neighbour can be assessed. Heterobimetallic centres are known to occur in bovine erythrocyte superoxide dismutase (Cu-Zn)⁸² and cytochrome C-oxidase (Cu-Fe)⁸³.

The imidazole ring of the amino acid, histidine is a ubiquitous ligand in chemical and biological systems⁸⁴. It's conjugate base, the imidazolate ion, bridges copper (II) and Zn(II) in bovine erythrocyte superoxide dimutase⁸². An imidazolate bridge splitting and reformation cycle has been postulated⁸⁵ to occur during enzyme turnover in an effort to rationalize the role of zinc.

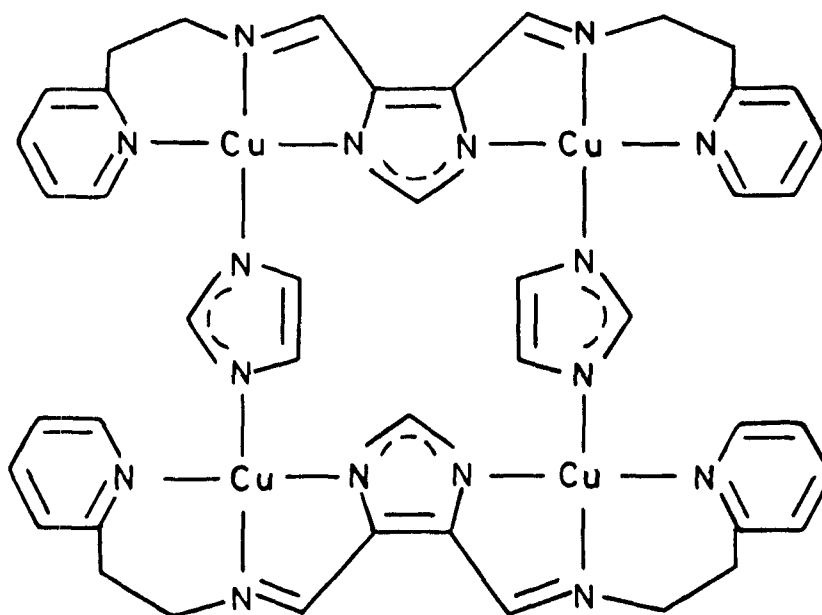
The imidazolate ion is known to bridge metal ions in polymeric or semipolymeric materials as uni-negative exobidentate ligand. The X-ray crystal analysis of $[\text{Cu}(\text{Iz})_2]$ ^{55,63} has indicated the formation of -Cu(1)-(Iz)-Cu(2)-(Iz)-Cu(1)-chains in crystal such that each Cu(1) atom has a flattened tetrahedral coordination and Cu(2) acquires a square coordination. The chains are linked at Cu(1) atoms to give rise to three-dimensional net work structure. Similar bridges between Cu(II) ions are shown^{62,86} to exist in semipolymeric $[\text{Cu}_3(\text{Iz})_2(\text{IzH})_8(\text{ClO}_4)_4]$ and in polymeric $[\text{Cu}(\text{Iz})(\text{IzH})_2\text{Cl}]$. The former consists of linear trinuclear clusters with unidentate (IzH) and (Iz) ion acts as an exobidentate ligand forming the Cu-Iz-Cu link. The crystal

contains one dimensional infinite Cu-Iz-Cu chains as shown in figure XVI.



(Figure-XVI)

Imidazolate bridging also exist in nonpolymeric complexes too and the first such example⁸⁷ is the tetramer $[\text{Cu}_2(\text{bpIz})(\text{Iz})_2(\text{NO}_3)_4 \cdot \text{H}_2\text{O}]$ (Figure XVII) where bpIz is 4,5-bis[2-(2 pyridyl)ethyliminomethyl]imidazolate. Magnetic susceptibility measurements^{87,88} of these complexes have revealed that Cu (II) ions are involved in antiferromagnetic exchange interactions propagated by the Iz ion bridge.



(Figure-XVII)

Some other discrete imidazolate bridged transition metal complexes e.g. $[\text{Cu}_2\text{bpIz}]^{3+}$ and $[\text{Cu}(\text{pip})_2](\text{Iz})^{3+}$ [pip=2-(2-pyridyl)ethyliminomethyl]pyridine) have also been reported^{87,88}.

It has, recently, been shown in this laboratory that imidazole can be substituted in BH_4^- anion yielding⁸⁹⁻⁹¹ novel moieties with B-N bonds. The reaction proceeds through elimination of hydrogen (s) depending on the stoichiometric ratio of the reactants to give dihydrobis, hydrotris or tetrakis (imidazolyl)borate anion formulated as $[\text{BH}_2\text{Iz}_2]^-$, $[\text{BHIz}_3]^-$ or $[\text{BIz}_4]^-$ respectively. These novel moieties have been found to exhibit⁸⁹⁻⁹⁴ considerable reactivity towards transition metal ions yielding stable complexes. The

physicochemical investigations on these compounds have confirmed that both pyridyl and pyrrolic nitrogens of the imidazole group in the poly (Imidazolyl) borate anions are involved in coordination to metal ions.

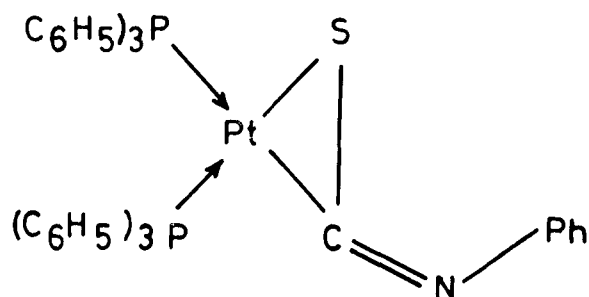
In coordination compounds with thiocyanate ion(s) as ligand, three possible modes of coordination of thiocyanate ion to a metal cation have been envisaged⁹⁵. These are (i) through nitrogen M-NCS (ii) through sulphur M-SCN and (iii) through both the nitrogen and sulphur when the SCN group is acting as bridges between two metal ions. The thiocyanate ligand is bifunctional with both, the nitrogen and sulphur atoms, equally potent to act as an electron pair donor. After coordination through the nitrogen end of the molecule, the sulphur end appears to be able to donate electrons in coordinate covalent bond formation with metal ions⁹⁶ like mercury(II) or silver(I). An analysis of the fundamental vibrations of the thiocyanate anion has been done by Penney and coworkers⁹⁷ who have assigned absorption band at 2053 cm^{-1} to this stretching mode. Chatt et. al.⁹⁸ have studied the number of thiocyanate complexes of palladium, platinum and silver and have shown that the C-N stretching frequency is found at higher wave numbers when the thiocyanate is bridging, than when it acts as monodentate coordinating ligand. The correlation⁹⁵ between infra-red band

frequency and structure, rather than to set up any definite diagnostic rules, could be summarized as:

- (1) The C-N stretching frequency is at higher wave numbers in the order M-NCS, M-SCN, M-SCN-M', all other factors are constant.
- (2) For a given disposition of the thiocyanate ion, the more polarizing the cation (the greater its charge or its electro-negativity or smaller the cation) the greater is the frequency of the C-N vibration.
- (3) Bridged thiocyanates are formed with a variety of strength, i.e. if the group M is sufficiently electro-positive it coordinates with the thiocyanate, forming an unsymmetrical bridge M-NCS-M' or M-SCN-M' and the frequency moves to much higher values.

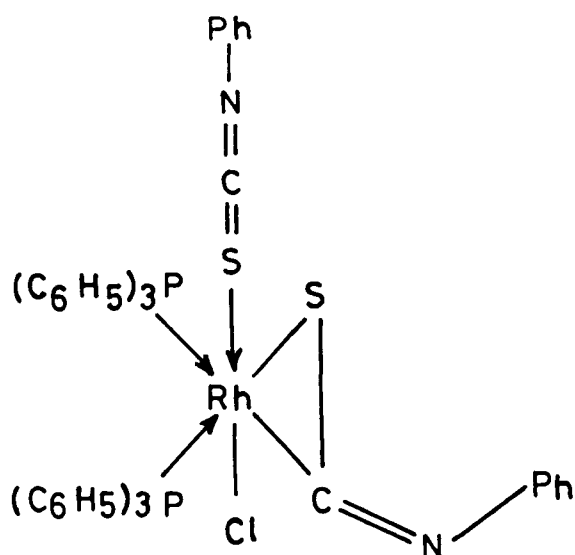
The organic isocyanates and isothiocyanates, RNCX (R=CH₃, C₂H₅, C₆H₅; X=O, S) are reported to be versatile Lewis bases⁹⁹ because of its ability to provide two or more possible donor sites for metal coordination and the large variety of organic moieties that can be varied in the R-position. The rubber industry has been issued several patents¹⁰⁰ on the use of RNCX with aluminium oxide, silicon oxide. Adducts formation of RNCX and iodine, phenol^{101,102} have been observed in solution. Adducts of RNCS with a few

transition metal ions with sulphur of the NCS moiety as potent coordinating site have been reported¹⁰³. Organic isothiocyanate have been shown¹⁰⁴ to coordinate through the C-S bond also, as represented by structure (Figure-XVIII).



(Figure-XVIII)

There is possibility of cis-trans isomerism about the C=N bond, but there is no evidence for the existence of such isomers. The $\nu(\text{C-N})$ stretching vibration characteristic of the C-S coordination as represented in figure XVIII is reported¹⁰⁵ to appear as a broad band at 1643 cm^{-1} about 450 cm^{-1} below the $\nu_{\text{asym}}(\text{NCS})$ vibration in free ligand. The structure as shown in figure -XIX has been proposed¹⁰⁴ for the complex $[\text{RhCl}(\text{PhNCS})_2\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]$ on the basis of i.r. spectral data.



(Figure-XIX)

There is comparatively less interest shown towards the synthesis of substituted isothiocyanate derivatives of non-metal atoms other than carbon, especially of P, As, Sb and Bi. The first non-metallic isocyanates¹⁰⁶ of phosphorus were actually reported as early as 1940, but until 1954 the substance in this class were difficult to prepare and practically no investigations had been carried out on them. The rapid development of this field began only with the discovery of simpler and more convenient methods of their preparation. General procedures for the preparation of non-metallic iso-thiocyanates other than carbon involve the reaction between the corresponding non-metal chloride and lead(II), mercury(II) or silver(I) thiocyanates^{107,108} either in benzene suspension or in the absence of the solvent. The use of silver thiocyanates in benzene suspension has been

extensively applied by Forbes and Anderson¹⁰⁹. Alkali metal or ammonium thiocyanates have also been used¹¹⁰ as suitable substituting agents, taking advantages of the solubility of ionic thiocyanates and the essential insolubility of the resulting alkali metal or ammonium chloride in organic solvents. It is possible for the thiocyanate (NCS) group in non-metal thiocyanates to bind the non-metal atom either through sulphur atom or the nitrogen atom. The preparation of typical addition compounds indicates that the reaction of potassium thiocyanate with substituted phosphorus chloride^{108,111}, acyl or aroyl chlorides¹¹² generate isothiocyanates. Analogous reaction between alkylhalides and potassium thiocyanate in ethanol, on the other hand have been shown to yield the corresponding normal thiocyanates¹¹³. It has been shown from the molar refraction measurements that phosphorus trichloride, phosphoryl chloride¹¹⁴ and the methyl chlorosilanes afford compounds with the isothiocyanate structure on treatment with metallic thiocyanates.

Phosphorus isocyanates are used for the preparation¹⁰⁶ of phosphorylated urethanes and ureas. Some of them are physiologically very active and have found practical use as insecticides and drugs. The phosphorus (III) isocyanates of the type $X_2\text{P(NCO)}$ and XP(NCO)_2 with $\text{X}=\text{Hal}$, alkoxy, aryloxy, alkyl and aryl are known¹⁰⁶. Phosphorus (V) isocyanates are very reactive and they can be prepared¹⁰⁶ from rapidly

obtainable starting materials. Phosphorus isocyanates in which halogen atoms are also attached to the phosphorus atom can react at two points in the molecule. They react very readily with alcohols, phenol, some amines and other compounds bearing active hydrogen and can therefore serve as important starting materials for the synthesis of derivatives of phosphoric acid and phosphinic acid.

Phosphorus(III) isocyanates often exhibit chemical properties¹⁰⁶ similar to those of phosphorus(III) chloride. The NCO groups show only a slight, if any, tendency to enter into addition reactions. Phosphorus(III) isocyanates decompose even in absence of air and moisture. Their stability¹⁰⁶ increases in the Series $P(NCO)_3 < ClP(NCO)_2 < Cl_2P(NCO)$.

Moreover, it was reported¹¹⁵ that organophosphorus(III) halides i.e. RPX_2 ($X=Cl, Br$) afford the corresponding isothiocyanate derivative when reacted under restricted condition with $AgSCN$, $Hg(SCN)_2$ or NH_4NCS . Furthermore, the preparative procedure required heating in each case usually under reflux in a suitable solvent and thiocyanato compounds of phosphorus are often thermally unstable. Fild¹¹⁶ found that further heating of freshly distilled $C_6F_5P(NCS)_2$ lead to complete transformation to a mixture of substances which could not be separated by distillation. From n.m.r. and other evidences he deduced that these were pentavalent phosphorus thiocyanato and cyano compounds i.e.



Dillon et. al.¹¹⁷ have carried out ^{31}P .n.m.r. spectral studies to illustrate the formation of $\text{RP}(\text{NCS})_2$ (R=alkyl, aryl or C_6F_5 species in solution.

These compounds are obtained as yellow coloured solutions in non-polar organic solvents, but are unstable in neat form and readily become viscous turning to a dark brown viscous liquid. While the methyl and ethyl compounds were even more unstable, quickly becoming reddish brown viscous liquid within the entry part of the inert atmosphere box. The most stable material was $\text{C}_6\text{F}_5\text{P}(\text{NCS})_2$, which had been isolated by Fild by distillation but further heating led to a mixture of two substances which could not be separated by distillation and gave higher field ^{31}P .n.m.r. signals at 7 and 40 ppm. These were deduced to arise from $\text{C}_6\text{F}_5\text{P}(\text{S})(\text{NCS})_2$ and $\text{C}_6\text{F}_5\text{P}(\text{S})(\text{CN})_2$ respectively.

CHAPTER-II

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

The characterization of coordination compounds is usually achieved by employing several available physico-chemical methods including spectroscopic techniques. The single crystal X-ray diffraction method (X-ray crystallography) has, during recent years, received a great deal of attention since it provides an accurate molecular geometry i.e. disposition of the constituent atoms in the molecules. A detailed discussion on the theory and practice of the various techniques are available in important text books, reviews and monographs, however, it seems appropriate to mention a brief account of the techniques which have been used in the investigations of the compounds described in the present work. The methods used are as follows:

1. Infra-red spectroscopy.
2. Nuclear magnetic resonance spectroscopy.
3. Electronic spectra (Ultra-violet and visible).
4. Magnetic susceptibility measurements.
5. Molar conductance measurements.
6. Molecular weight determination.
7. Elemental analyses.

Infra-red Spectroscopy:

Infra-red spectroscopy is the consequence of characteristic property of a compound and can be used to

reveal the structure and to provide information for new linkages or certain bond cleavage to establish the bonding sites in new compounds.

The vibrational and rotational-vibrational motion of a molecule are responsible for the absorption of energy. The rotational-vibrational absorption bands are usually found in gases and vibrational bands are found in condensed gases, liquids and solids.

Infra-red spectrum is commonly obtained by placing the sample in one beam of a double beam spectrophotometer and measuring the relative intensity of the transmitted (and therefore absorbed) light verses wavelength in wave numbers (per centimeter). The molecule can absorb all or part of the incident infra-red radiation increasing its natural vibration when the frequency of the incident radiation is the same as that of a given bond in the molecule and there is a change in the dipole moment during the vibration. As the molecule reverts from the excited state to the original ground state, the absorbed energy is released in the form of radiation. Radiation is absorbed and emitted only in discrete packets called photons.

A non-linear molecule has $3N-6$ degrees of freedom or modes of vibration (N is number of atoms) which results in a change in bond lengths or angles in the molecules. Normal modes are defined as to represent independent self repeating

motion in a molecule which is a harmonic oscillator. Sometimes these vibrational modes are less than the expected number, since the absorption of electromagnetic radiation in the i.r. region is possible only when there is a change in the dipole moment of the molecule during the normal vibration. If there is no such change it will be "infra-red inactive". For a particular vibration to be i.r. active the following selection rules have to be satisfied.

1. In order for a molecule to absorb infra-red radiation there must be a change in the dipole moment of the molecule as it vibrates.

2. In absorption of radiation only those transitions for which change in the vibrational energy level i.e. $\Delta V = \pm 1$ can occur or the energy of radiation must coincide with the energy difference between the excited and ground states of the molecule.

The frequencies of certain groups of atoms is called "group frequency". These frequencies are characteristic of the groups irrespective of the nature of the molecule in which these are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule. Stretching frequency can be related to the bond order. Thus stretching is higher for a triple bond as compared to a double bond and so on.

The i.r. spectrum contains absorption bands characteristic of the fundamental modes of vibration like stretching (symmetric and asymmetric) and bending or deformation (scissoring, wagging, twisting and rocking) and also those arising from multiples of fundamental frequencies (overtones) and/or sum or difference of some frequencies (combination bands).

In the following paragraphs only those frequencies which are pertinent to the discussion of the present compounds will be outlined.

-Si(CH₃)₃ stretching vibrations: Infra-red absorption bands arising from linkages involving silicon atoms are about five times more intense than the bands from the corresponding carbon linkages. In the series of open chain compounds examined by Wright and Hunter¹¹⁸ (the range from hexamethyl disiloxane to octadecamethyl octasiloxane) - Si(CH₃)₃ is observed as a strong band at 841 cm⁻¹ which decreases in intensity as the chain length is increased and which is uniformly absent from the corresponding cyclic compounds (hexamethylcyclo-trisiloxane). A second band whose intensity varies with chain length occurs in the same compounds at 756-754 cm⁻¹. These are clearly associated with vibrations involving the Si(CH₃)₃ end group of the open chain materials and would appear to be sufficiently characteristic for the identification of this grouping. This has been confirmed by

various workers¹¹⁹ from studies on a series of aryl trimethyl silanes which invariably show an intense band close to 840 cm^{-1} . Wright and Hunter noticed a band at 1258 cm^{-1} in their series of compounds. However, the additional band at 1250 cm^{-1} exhibited by tetramethylsilane¹²⁰ and other similar series of compounds, has been attributed to the rocking mode of the methyl grouping.

Si-N stretching vibration: The infrared and Raman spectra of Si-N compounds with structures containing SiNSi , SiN^{Si} and $(\text{-SiN-})_n$ units have been most studied¹²¹. The characteristic antisymmetrical Si-N (Si) stretching frequency lies in the range $900\text{-}1000\text{ cm}^{-1}$ while the symmetrical stretching frequency for the same group is in $400\text{-}600\text{ cm}^{-1}$ range¹²².

Imidazole ring vibrations: The i.r. spectra of pyrazole and imidazole are well known in the literature¹²³ for the several modes of these ligands. The infra-red spectra of 1:1 metal imidazole complexes in D_2O and corresponding spectra of imidazole and imidazolium ion have been discussed thoroughly. Band assignments have been ascertained by examining the infra-red spectra of the deuterated derivatives of imidazole and imidazolium ion. The in-plane bending and ring stretching modes of imidazole undergo sizable shifts to higher frequencies upon formation of imidazolium ion. The spectra of the metal complexes are more characteristic of free imidazole than of the imidazolium ion. These large frequency shifts in

imidazolium ion indicate that upon protonation (and to a lesser extent upon complex formation) the imidazole ring undergoes extensive π -electron redistribution. Ring stretching vibrations occur in the general region between 1600-1300 cm^{-1} . The absorption involves stretching and contraction of bonds in the ring and the interaction between these stretching modes. The band pattern and relative intensities depend upon the substitution and the nature of the substituents. Pyridine shows four bands while pyrroles display two to four bands in this region. Imidazole exhibits four strong bands¹²⁴ which occur at 1530 cm^{-1} (R_1 stretch.), 1480 cm^{-1} (R_2 stretch.), 1405 cm^{-1} (R_3 stretch.) and at 1330 cm^{-1} (R_4 stretch.). The characteristic pattern of absorption of the ring stretching vibrations result from the complete interaction of C=C, C=N and C-N and it is therefore, very difficult to isolate the different vibrations.

Stretching frequencies of $(\text{C}_6\text{H}_5)_3\text{P}$: Several reports dealing with infra-red and Raman spectroscopic investigations of primary, secondary and tertiary phosphines have appeared in literature¹²⁵ and complete vibrational analysis have been attempted. Tertiary phosphines containing the P-Ph linkage show two characteristic sharp absorptions of medium to weak intensity in the regions 1450-1425 cm^{-1} and 1010 cm^{-1} . Daasch and Smith¹²⁶ have examined a considerable series of aryl phosphorus compounds containing the P-aryl group and

have found in all cases bands in the region $1450-1435\text{ cm}^{-1}$ and $1005-995\text{ cm}^{-1}$ which are sharp and of moderate intensity. They associate these with P-Phenyl link but point out also that these might equally well arise from ring vibrations which have become activated in some way. Absorptions due to P-Phenyl has also been ascribed to bands at $520-420\text{ cm}^{-1}$ ¹²⁷.

-NCS stretching vibrations: The linear thiocyanate ion NCS^- exhibits three i.r. active fundamental vibrations which are, two stretching vibrations at 2060 cm^{-1} and 743 cm^{-1} associated with the C=N and C-S bands respectively and a deformation vibration at 470 cm^{-1} . However, it is well known that NCS^- ion can coordinate to metal ion through N as well as S centres. It has been of particular interest to obtain a reliable criterion to show whether bonding to the central metal ion be through the nitrogen atom (N- or iso series) or through sulphur atom (S- or normal series). The infra-red spectra of thiocyanato complexes have been extensively studied with this aim in view. Mitchell and Williams reported⁹⁵ the $\text{C}\equiv\text{N}$ stretching frequency to be usually higher in S-thiocyanates than in N-thiocyanates, though there are some exceptions. The C-S stretching frequency on the other hand, has been found to have the characteristic values of $860-780\text{ cm}^{-1}$ in N-thiocyanate complexes as opposed to Ca. 700 cm^{-1} in S-thiocyanato complexes¹²⁸. However it was emphasized by Sabatini and Bertini¹²⁹ that bonding in

thiocyanato complexes may be characterized by examining the N-C-S bending frequencies: N-bonded groups absorb at lower frequency. This criterion may be used to advantage when there are absorption bands in the region $700-850\text{ cm}^{-1}$ which can mask the weak C-S stretching band.

In derivatives like RNCS, R_3SiNCS , $\text{X}_{3-n}\text{P}(\text{NCS})_n$ ($\text{X}=\text{CH}_3$, C_6H_5 ; $n=1,2,3$) and even in HNCS the non metal atom (C, Si, P, H etc) are in general bonded to the N end of the NCS group yielding the isothiocyanates analogues. The three expected stretching frequencies of organic isothiocyanates have been approximated¹³⁰ as the R-N stretch, $\nu(\text{RN})$, the N-C stretch $\nu(\text{NC})$ and C-X stretch $\nu(\text{CX})$. These three modes would be expected to interact and mix with each other because of the extensive system and similarity in energy. In particular the N-C stretch and C-X stretch are known to be highly mixed, labelled as NCS asymmetric stretch $\nu_{\text{asym}}(\text{NCS})$ and NCS symmetric stretch $\nu_{\text{sym}}(\text{NCS})$ respectively. In RNCS the $\nu_{\text{asym}}(\text{NCS})$ has been reported at Ca 2100 cm^{-1} as a broad band. A medium to strong intensity band observed at Ca. 900 cm^{-1} is assigned to the characteristic of $\nu_{\text{sym}}(\text{NCS})$ stretching vibrations.

Metal-Nitrogen stretching bands: The M-N stretching frequency is of particular interest since it provides direct information about the coordinate bonds¹³¹. Because of the relatively heavy mass of the metal and the low bond order of

the coordinate bond the M-N stretching vibration may appear in the lower frequency region. Using metal isotope techniques Cornilsen and Nakamoto¹³² assigned the M-N stretching vibrations in sixteen imidazole complexes of Ni(II), Cu(II), Zn(II) and Co(II) which usually appear in the 325-210 cm^{-1} region. In series of papers, Powell¹³³ has examined a number of amine complexes in the rock salt and KBr regions (i.e. down upto only 450 cm^{-1}). He has reported extremely weak bands near 500 cm^{-1} , all of which were assigned to metal-nitrogen stretching frequencies.

P-N stretching vibration: The single bond P-N stretch frequency appear in the region 1050-1150 cm^{-1} while the P=N stretch frequency is reported to occur in 1300-1350 cm^{-1} , Niecke et al. reported¹³⁴ strong and broad bands for a P=N bond at 1345 cm^{-1} and 1298 cm^{-1} .

Metal-sulphur stretching vibration: The M-S stretching frequency generally appears as a single band of moderate intensity at Ca. 290 cm^{-1} . In some cases splitting of this band which are of weak to moderate intensity has also been reported¹²⁹.

Metal-halogen stretching frequency: The metal-halogen stretching vibration usually occurs in the far i.r. region (400-150 cm^{-1}). The M-X stretching frequency generally increases as the oxidation number of metal increases. It

depends on stereochemistry of the molecule also¹³⁵. It is inversely proportional to the mass of the metal.

The bands observed in the region $320\text{--}270\text{ cm}^{-1}$ in the present complexes are assigned to the terminal metal-halogen stretching bands. The bridging M-Cl-M stretching vibrations are reported to occur below 270 cm^{-1} ^{135,136}. The bridging halogen stretching vibrations are expected to appear in the lower spectral region as compared to the terminal one, which is reported¹³⁷ to occur in the region $305\text{--}290\text{ cm}^{-1}$.

Metal-phosphorus stretching vibration¹³⁸: The metal-phosphorus stretching vibration is located in the far i.r. region. The band is in general weak in intensity. For the present complexes they appear around $320\text{--}300\text{ cm}^{-1}$ spectral region.

Nuclear Magnetic Resonance:

Nuclear magnetic resonance spectrum is very helpful in ascertaining the structure of the compounds. Since the number of signals in an n.m.r. spectrum tells us how many kinds of protons a molecule contains.

The n.m.r. spectroscopy is most often concerned with nuclei with nuclear spin quantum number $I=1/2$, examples of which include ^1H , ^{31}P , ^{19}F . Spectra can not be obtained on nuclei with $I=0$ and only in special cases can spectra result from nuclei where $I \geq 1$.

A nucleus with $I=1/2$ when placed in an external field provides two allowed orientations i.e. $M_I = +1/2$ or $-1/2$ of the nuclear magnetic moment vector. The $+1/2$ corresponds to alignment of the vector with the applied magnetic field and $-1/2$ opposed to it. In the absence of a magnetic field all orientations of the nuclear moment are degenerate, but this degeneracy is lifted up in the presence of an external field in such a way that (for $I=1/2$) the $M_I = +1/2$ state will be lower in energy and the $-1/2$ state higher. The energy difference (ΔE) between the two states is not very high compared to the thermal energies kT .

When a molecule is placed in a magnetic field, its electrons are caused to circulate, and in circulating they generate secondary magnetic field i.e. induced magnetic fields. Circulation of electrons about the proton itself generates a field aligned in such a way that at the proton it opposes the applied field. The field felt by the proton is thus diminished and the proton is said to be shielded.

Circulation of electrons, specially π -electrons, about nearby nuclei generates a field that can either oppose or reinforce the applied field at the proton depending on the proton's location. If the induced field opposes the applied field, the proton is shielded as before. If the induced field reinforces the applied field, then the field felt by

the proton is augmented and the proton is said to be deshielded.

Compared with a naked proton a shielded proton requires a higher applied field strength and a deshielded proton requires a lower applied field strength to provide the particular effective field strength at which absorption occurs. Shielding thus shifts the absorption upfield and deshielding shifts the absorption down field. Such shifts in the position of the n.m.r. absorption arising from shielding and deshielding by electrons are called chemical shifts.

The units in which a chemical shift is most conveniently expressed is parts per million (ppm) of the total applied field. The reference point from which chemical shifts are measured is the signal from, usually tetramethylsilane $(\text{CH}_3)_4\text{Si}$. Because of the low electronegativity of silicon, the shielding of the protons in the silanes is greater than in most other organic molecules, as a result most n.m.r. signals appear in the same direction for the tetramethylsilane signal i.e. downfield.

The most commonly used scale is the δ (delta) scale. An n.m.r. signal from a particular proton appears at a different field strength than the signal from tetramethylsilane. This difference in chemical shift is measured in the equivalent frequency units ($\nu = \gamma H_0/2\pi$) and it is divided by the

frequency of the spectrometer used. Thus for a spectrometer at 60 MHz that is $60 \times 10^6 \text{ Hz}$.

$$\delta = \frac{\text{observed shift (Hz)} \times 10^6}{60 \times 10^6 \text{ (Hz)}}$$

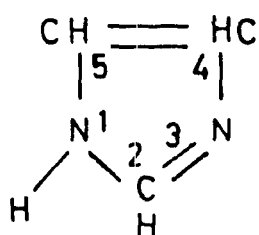
The chemical shift for a proton is determined, then, by the electronic environment of the proton. In a given molecule, non-equivalent protons have different chemical shifts while protons with the same environments i.e. equivalent protons have the same chemical shift.

The area under an n.m.r. signal is directly proportional to the number of protons giving rise to the signal. Areas under n.m.r. signals are measured by an electronic integrator and are usually given on the spectrum in the form of a stepped curve.

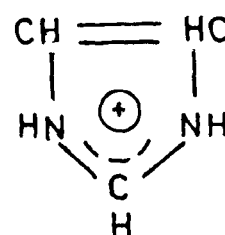
The fine structure of the peaks arises from the phenomenon known as spin-spin splitting and separation 'J' between the peaks comprising the fine structure is referred to as the spin-spin splitting constant.

The proton resonance spectra of 1:1 Zn(II) and Cd(II) imidazole complexes are reported¹²³ along with the corresponding spectra of imidazole and imidazolium ion. Each of these spectra shows a simple first order AX_2 pattern in D_2O consisting of two peaks in the intensity ratio 1:2. The less intense peak is assigned to the proton at C-2

(Figure-XX) while the other is assigned to the C-4 and C-5 protons, magnetically equivalent in solution because a rapid N-H proton exchange takes place with solvent. It is for this reason also that the NH proton of imidazole does not show a separate resonance in aqueous solution.



Imidazole



Imidazolium ion

(Figure-XX)

Nuclear magnetic resonance spectroscopy has proved to be a very valuable tool for the identification and characterization of primary, secondary and tertiary phosphines. Hydrogen directly attached to phosphorus causes splitting of the shift by interactions of the hydrogen nucleus with the ^{31}P nucleus. Thus in ^{31}P n.m.r. primary phosphines exhibit three peaks with the relative intensities of 1:2:1 and secondary phosphines 2 peaks with the relative intensities of 1:1. Tertiary phosphines give only one peak¹²⁷.

The ^1H n.m.r. spectrum of triethylphosphine indicates that the lone electron pair of the phosphorus may be involved in the chemical bonding of the ethyl group to phosphorus. The ^1H n.m.r. spectrum of triphenyl phosphine is also reported¹³⁹.

Electronic Spectra (Ultra-Violet and Visible Spectroscopy):

Most compounds absorb light somewhere in the spectral region between 200 and 1000 nm. The absorption of these radiations cause electronic excitation of the molecule to higher electronic states. The spectra observed in this region are often called electronic spectra.

Electronic transitions in transition metal complexes has been well accounted in terms of ligand field theory. Ligand field theory provides a simple model for the elucidation of structure of transition metal complexes. In a transition metal, all the five 'd' orbital viz. dxy, dyz, dxz, d_{z^2} and $d_{x^2-y^2}$ are degenerate. However in coordination compounds due to the presence of ligands, this degeneracy is lifted and d orbitals split into two groups called t_{2g} (dxy, dyz and dxz) and eg (d_{z^2} and $d_{x^2-y^2}$) in an octahedral complex and t_2 and e in a tetrahedral complex. The set of t_{2g} orbitals goes below and eg orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two

sets of orbitals is reversed, the e going below and t going above the original degenerate level.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon "Russel-Saunders Scheme" must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorically add upto zero. The total orbital angular momentum (L) is obtained by adding l value of the individual electrons, which are treated as a vector with the component m_l in the direction of the applied field. Thus,

$$L = \sum l_i = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

S P D F G H I

The total spin angular momentum $S = \sum s_i$ where s_i is the value of spin angular momentum of the individual electrons. S has degeneracy equal to $2S+1$, which is also known as "spin multiplicity".

In general the terms or spectroscopic symbols arising from a d^n configuration are as follows:

$$d^1 \text{ or } d^9 : {}^2D$$

$$d^2 \text{ or } d^8 : {}^3F, {}^3P, {}^1G, {}^1D, {}^1S$$

$$\begin{aligned}
d^3 \text{ or } d^7 &: {}^4F, {}^4P, {}^2H, {}^2G, {}^2F, {}^2D(2), {}^2P \\
d^4 \text{ or } d^6 &: {}^5D, {}^3H, {}^3G, {}^3F(2), {}^3D, {}^2P(2), {}^1I, {}^1G(2), \\
&{}^1D(2), {}^1S(2) \\
d^5 &: {}^6S, {}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G(2), {}^2F(2), \\
&{}^2D(3), {}^2P, {}^2S \\
d^0 \text{ or } d^{10} &: {}^1S
\end{aligned}$$

Coupling of L and S also occurs because both L and S if non zero, generate a magnetic field and thus tend to orient their moments with respect to each other, in the direction where their interaction energy is least. This coupling is known as 'L-S coupling' and give rise to the resultant angular momentum denoted by the quantum number J which may have quantized positive values from L+S upto L-S. Each state specified by J is 2J+1 fold degenerate. The total number of states obtained from a term is called the multiplet and each value of J associated with a given value of L is called a component. Spectral transitions due to spin-orbit coupling in an atom or an ion occurs between the components of two different multiplets. While L-S coupling scheme is used for the elements having atomic number less than 30. However for heavy elements in whose case spin-orbit interactions are large and electronic repulsion parameters decreases the spin angular momentum of an individual electron couples with its orbital momentum to give an individual j for that electron.

The individual j 's couple to produce a resultant J for the atom.

The electronic transition taking place in an atom or ion are governed by certain "Selection Rules" which are as follows:

- (1) Transition between states of different multiplicity are forbidden.
- (2) Transitions involving the excitation of more than one electron are forbidden.
- (3) In a molecule which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

The ground term of a d^n system is the one which has the highest spin multiplicity and the highest L value. All the terms of a given system further split in the presence of a ligand-field. Inter-electronic repulsions within a configuration give the energies of the terms above the ground term. The energies are function of two parameters related to electron repulsion. The two parameters may be chosen in either the way of Condon and Shortley (F_2 , F_4) or in that of Racah (B and C) for d orbital electrons. For the first transition series ions the value of C/B is around 4.0 and B is about $1,000 \text{ cm}^{-1}$. It is possible to examine the effects of crystal field on a polyelectronic configuration. The ligand-

field splitting due to cubic field can be obtained by consideration of group theory. It has been shown that an S state remains unchanged, P state does not split, a D state splits into two and F state into three and a G state into four states as tabulated below. This holds for a octahedral (Oh) as well as tetrahedral geometry.

S	————	A_1
P	————	T_1
D	————	$E + T_2$
F	————	$A_2 + T_1 + T_2$
G	————	$A_1 + E + T_1 + T_2$

In weak crystal fields the inter-electronic repulsions are larger. The crystal field may, however, be of comparable magnitude (medium strength) or it may be larger than the inter, electronic repulsions.

Correlation diagram for free ion (weak field) strong field configuration from $d^1 - d^9$ for both octahedral and tetrahedral cases are available. In addition to the qualitative aspects of transition from weak to strong crystal-fields it is also necessary to have quantitative results available for the interpretation of spectra. The so called Tanabe-Sugano diagrams make it possible. In these diagrams, the energies of the levels of a d^n system as E/B are plotted as the vertical coordinate and the crystal field strength in the form of Dq/B as the horizontal coordinate.

This diagram requires two parameters B and C for the inter-electronic repulsions. It can be drawn only if the ratio C/B is specified.

Transition from the ground state to the excited state occur according to selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultra-violet region of the spectrum. Such spectra are known as 'charge transfer spectra' or redox spectra. For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transitions. However, these should be clearly discerned from the ligand bands which might also occur in the same region.

The spectra of transition metal complexes may be recorded in the solid state as well as in the solution. A single crystal may be studied in which case the observation of the absorption spectrum is made in different crystal orientations and with light polarized in different planes.

The diffused reflectance spectrum is helpful in assigning the possible geometry of the complexes in condensed phase. In this technique the sample is ground

finely and the light reflected from it is examined. It is usually advantageous to grind the compound with a suitable inert white material, such as magnesium oxide. Minima in the reflected light occur at the absorption bands of the complex. Unless the grinding is very thorough the band obtained in diffused reflectance spectra tend to be broader and show less structure than the one recorded in solution or as a simple crystal for the same complex. However often diffuse reflectance spectrum is the only method available for the study of the spectrum of an insoluble material. The spectrum represents plot of relative absorbance against energy.

It is appropriate to discuss in brief the assignments of various bands vis-a-vis to geometry of the molecule through discussing the electronic spectra of several complexes with transition metal ions pertinent to this work.

d^1 and d^9 : In both these cases if the perturbing field is perfectly cubic then there is only one transition ${}^2E_g \rightarrow {}^2T_{2g}$ (reversed for d^9)¹⁴⁰. Usually there are other perturbations present which change the simple concept of one band in the visible and near ultra-violet region. Both d^1 and d^9 have Jahn-Teller effects which may distort the perfectly octahedral structures at least tetragonally and in addition for d^9 the spin-orbit coupling has become Ca. 800 cm^{-1} so

that this will impose a further perturbation upon the previous one. The excited E_g level in d^1 , under the influence of a tetragonal perturbation would split into $B_{1g} + A_{1g}$ levels. A rough estimate of the split from an examination of the band envelope shape for aqueous Ti(III) spectra suggests a value of perhaps $2,000\text{ cm}^{-1}$ so that the transition is from an essentially octahedral ${}^2T_{2g}$ level to a tetragonal pair ${}^2B_{1g}$ and ${}^2A_{1g}$. Copper(II) hexahydrate exhibits a single broad maximum at $12,600\text{ cm}^{-1}$ but the envelope may be visualized to contain more than one transition. Four coordinate copper(II) complexes are also known, and the CuCl_4^{-2} ion appears from its spectrum to be nearer to square than tetrahedral but there are often interactions with the solvent which cloud the issue. It does not seem to be a valid assumption that this species is perfectly tetrahedral.

d^2 and d^8 : Vanadium (III) is a case of d^2 configuration. This oxidation state was one of the first to be treated by Hartmann et al¹⁴¹. Both the hexahydrate and the tris oxalato complexes have well defined transitions at $17,000\text{ cm}^{-1}$ and $24,000\text{ cm}^{-1}$ and these are now assigned as ${}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$. The second transition was originally assigned as ${}^3A_{2g}(F) \leftarrow {}^3T_{1g}$ but this is unlikely as configurationally, it represents $eg^2 \leftarrow t_{2g}^{9/5} eg^{1/5}$ i.e. a 'two' electron transition.

The spectra of nickel (II) complexes are among the most exhaustively investigated for many reasons, one of them being the large spin-orbit coupling constant.

The octahedral Ni(II) complexes usually exhibit a band in the infra-red at $8,600\text{ cm}^{-1}$ with a close pair of bands in the red ($\sim 14,000\text{ cm}^{-1}$) followed by somewhat weaker band at $18,500\text{ cm}^{-1}$ and a comparatively stronger transition in the blue at $25,500\text{ cm}^{-1}$ which has been assigned as

${}^3T_{2g}$	<----	${}^3A_{2g}$	at $8,600\text{ cm}^{-1}$	
${}^3T_{1g}(F)$	<----		at $13,500\text{ cm}^{-1}$	
${}^1E_g(D)$	<----		at $15,400\text{ cm}^{-1}$	
${}^1A_{1g}(G)$	<----		at $18,500\text{ cm}^{-1}$	
${}^3T_{1g}(P)$	<----		at $25,500\text{ cm}^{-1}$:

By elongating one of the axes of an octahedral complex, the limiting structure of the complex will be a square-planar configuration. This structure would produce a diamagnetic Ni(II) complex. However, as shown by Ballhausen and Maki¹⁴², it is by no means certain. A very weak square-planar crystal field will still produce a paramagnetic complex. Similar conclusions have been reached independently by Hartmann and Fischer-Wasels¹⁴³. Condition for dia- and para-magnetism of square-planar nickel(II) complexes have been given by Ballhausen and Liehr¹⁴⁴ considering a strong crystalline field point of view.

If the triplet state is not too high in energy over the singlet ground state there is a possibility that it may be equally populated at ordinary temperatures or in other words the crossing over of the singlet and triplet states occur at ordinary temperatures and hence the complex should exhibit a weak temperature dependent paramagnetism.

d^3 and d^7 : Chromium(III) is the best known representative of d^3 and its spectrum with many different ligands is known. The ground state is $^4A_{2g}$ and is the only state of maximum multiplicity arising from the configuration t_{2g}^3 . The lowest lying terms of the free ion are 4F , 4P and 2G in that order and of the excited stark levels arising from them, six have so far been identified. They are -

2E_g	<-----	$^4A_{2g}$	at 15,000 cm^{-1} in the ruby spectrum.
$^2T_{1g}$	<-----		at 15,500 cm^{-1} in the ruby spectrum.
$^4T_{2g}(F)$	<-----		at 17,400 cm^{-1} in the hydrate spectrum.
$^2T_{2g}$	<-----		at 22,000 cm^{-1} in the ruby spectrum.
$^4T_{1g}(F)$	<-----		at 24,700 cm^{-1} in the hydrate spectrum.
$^4T_{1g}(P)$	<-----		at 37,000 cm^{-1} in the hydrate spectrum.

Cobalt(II) complexes may have a doublet ground state instead of a quartet but Dq never reaches a large enough value for the cross over to occur.

The known transitions are (for the octahedral molecules).

${}^4T_{2g}(F)$	<----	${}^4T_{1g}$	at 8-9,000 cm^{-1} .
2E_g	<----		at 11,000 cm^{-1} .
${}^4A_{2g}(F)$	<----		at 16-18,000 cm^{-1} .
${}^4T_{1g}(P)$	<----		at 20-21,000 cm^{-1} .

The ${}^2E_g \leftarrow {}^4T_{1g}$ transition is interesting in that it represents configurationally $t_{2g}^6 e_g^1 \leftarrow t_{2g}^5 e_g^2$ and so should be broad and its maximum should shift to lower frequencies with decreasing temperature because its energy curve plotted against Dq has a larger negative slope than the curve for the ground term. The ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ should be expected to be much weaker than the other transition because it corresponds to a two electron excitation which is, quantum mechanically, a forbidden transition.

Tetrahedral cobalt complexes (in particular $[\text{CoCl}_4]^{-2}$) are well known and their spectra have been interpreted on CF theory. Their intensities are about 10^2 times that of the octahedral. The ground state here is ${}^4A_2 (e)^4 (t_2)^3$, and three quartet transitions are expected to occur.

d^5 :

Manganese (II) has been exhaustively investigated in its complexes with many ligands. The hexa hydrate is an example and its assignments are given below.

${}^4T_{1g}(G)$	<-----	${}^6A_{1g}$	at 18,800 cm^{-1} .
${}^4T_{2g}(G)$	<-----		at 23,000 cm^{-1} .
${}^4E_g(G)$	<-----		at 24,900 cm^{-1} .
${}^4{}_{1g}(G)$	<-----		at 25,150 cm^{-1} .
${}^4{}_{2g}(D)$	<-----		at 28,000 cm^{-1} .
${}^4E_g(D)$	<-----		at 29,700 cm^{-1} .
${}^4T_{1g}(P)$	<-----		at 32,400 cm^{-1} .
${}^4A_{2g}(F)$	<-----		at 35,400 cm^{-1} .
${}^4T_{1g}(F)$	<-----		at 36,900 cm^{-1} .
${}^4T_{2g}(F)$	<-----		at 40,600 cm^{-1} .

Ruthenium has the electronic structure $(4d)^7 (5s)^1$. Complexes with the metal in the oxidation states two to six are found. Ru(II) has the electronic structure $[\text{Kr}] (4d)^6$ eg. $\text{Ru}(\text{CN})_6^{4-}$ is colourless and presumably diamagnetic.

Ru(III) complexes on the other hand are fairly well characterized. The electronic structure corresponds to d^5 . Spectra of the red species RuCl_6^{3-} and RuBr_6^{3-} have been given by Jørgenson¹⁴⁵. The work of Hartmann and Buschbeck¹⁴⁶ describes spectra of RuCl_6^{3-} , of the colourless $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and of the red violet complex $[\text{Ru}(\text{NH}_3)_5\text{I}]^{+2}$.

Magnetic Susceptibility:

It has been well indicated that the determination of magnetic moments of transition metal complexes provide ample information in assigning their structure. The orbital

splitting patterns derived from ligand field theory for transition metal complexes of the first transition series provide a reliable first-order-interpretation (particularly in understanding the number of unpaired electrons) of the measured magnetic susceptibilities. The main contribution to bulk magnetic properties arises from the magnetic moment resulting from the motion of the electrons. It is possible to calculate the magnetic moments of compounds from the measured values of magnetic susceptibility.

Substances can be classified into four distinct classes depending on the magnetic behaviour as diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic.

Diamagnetism is shown by the compounds containing paired electrons. A diamagnetic substance, when placed in a magnetic field aligns itself perpendicular to the direction of the field, so as to allow minimum number of magnetic lines of force to pass through it and there is a net loss in its weight. Furthermore, the applied field induces motion of electrons in such a direction so as to generate a magnetic moment which is opposed to it and hence the diamagnetic substances are repelled by a magnetic field. The dia-magnetic effect is a temporary effect and exists only in the presence of magnetic field and vanishes as soon as the magnetic field is removed.

Paramagnetism is shown by the substances containing unpaired electrons. Paramagnetic substances are more permeable to the magnetic lines of force, so align themselves parallel to the direction of the applied field and large number of lines of force can pass through them. Consequently there is a net gain in the weight of the paramagnetic substances when kept in a magnetic field. The field induces motion of the electron in a direction so as to produce magnetic moment which is in the direction of the applied field. It is a permanent effect and exists even in the absence of field.

Substances in which the electron of the adjacent paramagnetic sites interact magnetically with each other are ferromagnetic or antiferromagnetic. A ferromagnetic substance is one in which the adjacent magnetic dipoles are oriented in the same direction. An antiferromagnetic material is one in which adjacent magnetic dipoles are oppositely oriented.

For determining magnetic moment of a substance, magnetic susceptibility is measured from which magnetic moment can be calculated.

Magnetic susceptibility, χ may be defined as the ratio of intensity of magnetization (I) induced in a substance to the strength of applied magnetic field(H).

$$\chi = \frac{I}{H} = k \quad \dots (7)$$

k is called the magnetic susceptibility per unit volume.

This is simply related to both the gram susceptibility, χ_g and molar susceptibility χ_M

$$\chi_g = \frac{k}{d} \quad \dots (8)$$

$$\chi_M = \frac{k}{d} \cdot M \quad \dots (9)$$

where d and M are the density and molecular weight of the substance.

The magnetic susceptibility is a dimensionless quantity which is positive for paramagnetic and negative for diamagnetic substances. However, paramagnetic substances have a negative diamagnetic contribution to their net susceptibility. So for determining correct magnetic susceptibility, a diamagnetic correction is possible.

$$\chi_M^{\text{corr}} = \chi_M - \chi_{\text{dia}} \quad \dots (10)$$

In general magnetic susceptibility depends on temperature, within a certain limit of temperature range (20-40K). The dependence of χ_M^{corr} upon temperature is given by

$$\chi_M^{\text{corr}} = \frac{C}{T - \theta} \quad \dots (11)$$

where θ = Curie-Weiss constant and

C = Curie constant

Curie constant has the value

$$C = \frac{N}{3k} (\mu_{\text{eff}})^2 \beta^2 \quad \dots (12)$$

where N = Avagadro's number

k = Boltzman's constant

μ_{eff} = Effective magnetic moment

β = Bohr magneton.

The effective magnetic moment is a quantity of considerable interest to chemists, which after the substitution of the value of the constants can be represented as

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot T} \quad \dots (13)$$

The magnetic proportion of any individual atom or ion results from the combination of spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus (classical way), however the contribution due to orbital moment is very small.

For a free paramagnetic ion, the effective magnetic moment may be calculated from the formula,

$$\mu_{\text{eff}} = g [J(J+1)]^{1/2} \quad \dots (14)$$

where g = Lande's spectroscopic splitting factor and is given by the formula

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \dots (15)$$

where J, L, S refer to the ground state spectroscopic terms.

In the compounds of first transition series the orbital contribution to the magnetic moment is almost completely quenched by the ligand field. Therefore, substituting $L=0$ and $J=S$ in equation (14) and (15), thereby obtaining $g=2$ and the following spin-only formula which may be used for appropriate calculation of μ_{eff} .

$$\mu_{\text{eff}} = 2[S(S+1)]^{1/2} \quad \dots (16)$$

This equation is significant in study of the transition metal complexes, because the number of unpaired electrons may be correlated with the bonding or structure of the complexes.

There are three different methods, namely Gouy's method, Evan's method, Faraday's method which are used for the measurement of the magnetic susceptibility of the complexes. Faraday's method can be applied for the samples which are too small for the Gouy method.

The gram susceptibility is measured by the following formula,

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{\text{Std}}}{\Delta W_{\text{Std}}} \cdot \chi_{\text{std.}} \quad \dots (17)$$

where χ_g = gram susceptibility

ΔW = change in weight of the unknown sample with magnet on and off

W = Weight of the known sample

ΔW_{std} = Change in weight of standard sample with magnets on and off.

$W_{\text{std.}}$ = weight of standard sample

$\chi_{\text{std.}}$ = Gram susceptibility of the standard sample.

The magnetic moment is usually expressed in B.M. (Bohr Magneton) which may be defined as.

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

where,

e = electronic charge

h = Planck's constant

m = mass of the electron

c = velocity of light

The magnitude of μ_{eff} is then measured using expression defined above by equations (9), (10) and (13).

Molar Conductance:

The magnitude of molar conductance give direct information about the ionic and non ionic nature of a given compound and is therefore, considered a simple and easily accessible method for the characterization of coordination compounds.

Ohm's law states that current strength I is directly proportional to the applied electromotive force (emf, E) and inversely proportional to the resistance (R)

$$I = \frac{E}{R} \quad \dots (18)$$

The resistance of any uniform conductor varies directly as its length [$l(\text{cm})$] and inversely as its area of cross section [$a(\text{sqcm})$], so that

$$R = \rho \frac{l}{a} \quad \dots (19)$$

where ρ , a constant for a given conductor is known as the specific resistance or resistivity, its units are ohm cm. The specific conductance of any conductor is defined as the reciprocal of the specific resistance and may be represented by symbol k . The conductance, ' C ' is defined as the reciprocal of the resistance so that by equation (19).

$$C = K \frac{a}{1} \text{ ohm}^{-1} \quad \dots (20)$$

Kohlrausch defined a function called the equivalent conductivity (Λ)

$$\Lambda = 1000 \frac{K}{C} \text{ ohm}^{-1} \text{ cm}^2 \quad \dots (21)$$

where C is the concentration of the solution in gram equivalent per litre.

The following relation is used for determining the molar conductance (Λ_M)

$$\Lambda_M = \frac{\text{Cell constant} \times \text{conductance}}{\text{Concentration of solution}} \quad \dots (22)$$

Usually solutions of $1 \times 10^{-3} \text{ M}$ strength are used for the conductance measurements. Molar conductance¹⁴⁷ value of different type of electrolytes in a few solvents are given below.

Solvent	Molar Conductance ($\text{Ohm}^{-1} \text{ cm}^2$)	Type of electrolyte
Nitromethane	75-95	1:1
DMSO	50-75	1:1
DMF	65-90	1:1
Methanol	80-115	1:1
Nitromethane	150-180	1:2
DMF	130-170	1:2
Methanol	160-220	1:2

Molecular Weight Determination:

Molecular weight determination is useful for deciding the composition of a molecule. Various methods are available to determine the molecular weight of a given compound.

1. Osmotic pressure method
2. Sedimentation method
3. Light scattering method
4. Viscosity method
5. Rast method

Viscosity method and Rast method have been used to determine the molecular weight of the compounds in the present work.

Viscosity method: The method commonly employed is based on Poiseuille's law which connects the rate of flow of a liquid through a capillary tube with the coefficient of viscosity of the liquid and is expressed by equation,

$$\eta = \frac{\pi r^4 t p}{8 v l} \quad \dots (23)$$

where v is the volume in ml of the liquid flowing in t seconds through a narrow tube of radius r cm and length l cm. under a hydrostatic (driving) pressure of p dynes per square centimeter and η is the coefficient of viscosity in poise.

Since the hydrostatic pressure P of a liquid column is given by

$$P = hdg \quad \dots (24)$$

where h is the height of the column and d the density of the liquid, the Poiseuille's equation (23) may be written as

$$\eta = \frac{\pi r^4 t h d g}{8 v l} \quad \dots (25)$$

It is not necessary to measure all the quantities on the right hand side of the above equation. The viscosity of water at different temperatures has been very accurately determined. The usual procedure is to determine the viscosity of a liquid with reference to that of water. This is termed as relative viscosity. The time of flow for equal volumes of water and the liquid under the examination through the same capillary is measured. If t_1 and t_2 are the times of flow of the same volumes of water and liquid respectively and η_1 and η_2 are their respective coefficient of viscosity then

$$\frac{\eta_1}{\eta_2} = \frac{\pi r^4 t_1 h d_1 g}{8 v l} \times \frac{8 v l}{\pi r^4 t_2 h d_2 g} \quad \dots (26)$$

The value of h will be the same in both cases since equal volumes of both liquids were taken and they will stand at the same height

$$\therefore \frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \dots (27)$$

where d_1 and d_2 are the densities of water and liquid respectively.

The Ostwald's viscometer is used for measuring viscosity by above method.

$$\text{Similarly } \frac{\eta_2}{\eta_3} = \frac{d_2 t_2}{d_3 t_3} \quad \dots (28)$$

where η_3 , d_3 and t_3 are viscosity, density and time of flow of the solution respectively.

Knowing the coefficient of viscosity of water (η_1) of solvent (η_2) that of the solution (η_3) can be calculated by the relation (27) and (28).

Viscosity of a solution is related¹⁴⁸ to its density by the following equation.

$$\eta_3 = K_3 d_3 t_3 \quad \dots (29)$$

where K is a constant

Specific viscosity η_{sp} is given by relation.

$$\eta_{sp} = \frac{\eta_{\text{solution}} - \eta_{\text{solv}}}{\eta_{\text{solv}}}$$

$$\text{i.e. } \eta_{sp} = \frac{\eta_3 - \eta_2}{\eta_2} \quad \dots (30)$$

Specific viscosity¹⁴⁸ is related to the molecular weight of the compound by the equation

$$\eta_{sp} = MK_3C \quad \dots (31)$$

$$\text{or } M = \frac{\eta_{sp}}{K_3C} \quad \dots (32)$$

where C is concentration in gm/ml knowing the K_3 and η_{sp} from equation (29) and (30) respectively, the molecular weight of a compound can be calculated by using equation (32).

Rast Method¹⁴⁹:

A weighed amount of the compound was mixed with about 10 times its weight of camphor and the whole mixture was melted and the whole mixture was finely grinded and some quantity was transferred to capillary tube. The point at which the last trace of camphor was about to be completely melted, was recorded as the freezing temperature of the solution. The depression of the freezing point from that of pure camphor was determined with sufficient accuracy and then molecular weight of the compound was calculated by using the following formula

$$M = K \frac{1000 W}{Tw} \quad \dots (33)$$

where

M = Molecular weight of the compound

K = Mol. depression constant of camphor (39.7)

W = Weight of the compound taken

T = Difference in freezing temperature

w = Weight of the camphor taken

Elemental Analyses:

The chemical analyses is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. The microanalysis of carbon, hydrogen, and nitrogen were done on a Coleman analyser at the Microanalytical laboratory of the Science College Calcutta. The estimation of halogen (chloride) was done gravimetrically¹⁵⁰. A known amount of the sample was fused with a fusion mixture containing KNO_3 and K_2CO_3 in a nickel crucible. The mixture was then dissolved in a very dilute nitric acid. Silver chloride was precipitated by the addition of an excess of silver nitrate solution to the chloride solution. The precipitate was collected in a weighed sintered crucible, washed, dried at $100-200^\circ\text{C}$ and finally weighed as silver chloride. Metal analysis were carried out by chelometric titration with standard EDTA¹⁵¹. For the metal estimation, a known amount of complex was

decomposed by the addition of a few drops of a mixture of nitric acid, sulphuric acid and perchloric acid and this metal solution was titrated against standard EDTA solution. Tin was estimated as SnO^{152} .

CHAPTER-III

STUDY OF REACTIONS OF N-TRIMETHYLSILYLIMIDAZOLE
AND N-TRIMETHYLSILYL-2-METHYLIMIDAZOLE TOWARDS
ANHYDROUS METAL CHLORIDES AND THEIR
DERIVATIVES; SYNTHESIS AND PHYSICO-CHEMICAL
STUDIES ON Co(II), Ru(II), Ru(III) AND Cu(II)
IMIDAZOLATES AND MIXED LIGAND IMIDAZOLATES

INTRODUCTION

Transition metal complexes of imidazole have been the subject of considerable investigations during the last two decades because they are models for histidyl residues of proteins or of bovine erythrocyte superoxide dismutase. Attempts by previous workers^{49,79} to prepare imidazolate complexes of first row transition metals employing transition metal salts and imidazole in aqueous media in the presence of KOH have yielded polymeric substances which neither melt nor dissolve in any solvent. It has, recently, been shown¹⁵³ that transition metal chlorides like VCl_4 , WCl_6 , MoCl_5 and VOCl_3 under anhydrous conditions are attacked by bis(trimethylsilyl)sulphurdiimide $(\text{Me}_3\text{SiN})_2\text{S}$ yielding novel oligomeric species $(\text{Cl}_n\text{MN}_3\text{S}_2)_x$ with covalent M-N bonds which under suitable crystallizing condition yield monomeric or dimeric form of metallacycles with delocalized π -electrons in the ring. It was therefore, considered imperative to look for a N-silylated derivative of imidazole which may be exploited as a reagent for preparation of monomeric transition metal imidazoles. It has been found that N-trimethylsilylimidazole and N-trimethylsilyl-2-methyl-imidazole are potent reagents for the synthesis of monomeric imidazolato complexes which melt sharply and are soluble in most organic solvents. The reactivity of the trimethylsilyl group in N-trimethylsilylimidazole towards

C-Cl bonds of organic substrate to form the corresponding N-substituted imidazole derivatives is quite well known^{154,155}. However, to our knowledge no report has appeared in the literature regarding the reactivity of N-trimethylsilyl-imidazole towards M-Cl bonds.

This chapter describes the results of the studies on the reactivity of the reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole towards CoCl_2 , RuCl_3 , CuCl_2 and a few of their derivative complexes e.g. $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$, $[\text{Cu}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}]$, $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}_2]$ and $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}_2\text{Cl}_3 \cdot \text{MeOH}]$. The newly obtained compounds have been characterized by elemental analyses, molecular weight and magnetic susceptibility measurements and i.r., reflectance and electronic spectral studies.

EXPERIMENTAL

Reagents Used:

The reagents triphenylphosphine (S.R.L.), imidazole (Loba), 2-methylimidazole (S.R.L.), hexamethyldisilazane (S.R.L.), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Glaxo-India), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (E.Merck), RuCl_3 (B.D.H., England), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey Chemicals Ltd., London), glacial acetic acid (S.D. Fine Chemicals Ltd., India), sulphuric acid (B.D.H., England), ammonia solution (B.D.H., England) were commercial pure samples and used as such. Solvents like tetrahydrofuran, benzene, pet.-ether, dichloromethane, *n*-hexane, dimethylsulfoxide, (all reagent grade) were dried before use by literature method¹⁵⁶.

PREPARATION OF THE PRECURSORS:

Preparation of N-trimethylsilylimidazole¹⁵⁷: Hexamethyldisilazane (12.1 gm, 75.0 mmol) was taken in a round bottomed flask fitted with a reflux condenser and drying tube. Dry nitrogen was flushed in to expel air, acidified and then imidazole (6.8 gm, 100.0 mmol) was added. Vigorous reaction took place and it was refluxed for 2-3 hrs. to ensure no more NH_3 is evolved, then fractionally distilled under vacuum. The fraction distilling at 92°C and 12 torr. were collected. The purity of the reagent was checked by i.r. and ^1H n.m.r. spectra.

Analyses calculated for $\text{C}_6\text{H}_{12}\text{SiN}_2$; C, 51.40; H, 8.62; N, 19.97; observed 51.09, 8.15, 19.89 respectively; i.r.

3145m, 3125m, 1549m, 1480s, 1440m, 1330s, 1260s, 1165s, 1060s, 930m, 850s, 770s, 750s, 670s, 620s cm^{-1} ; ^1H n.m.r. 0.85 δ (9H), 6.8 δ (2H) and 7.61 δ (1H).

Preparation of N-trimethylsilyl-2-methylimidazole: It was prepared in the same manner as described above by taking 2-methylimidazole (7.2 gm, 87.0 mmol) and hexamethyldisilazane (10.5 gm, 68.0 mmol). The crude was fractionated and the fraction distilling at 180°C and 20 torr was collected.

Analyses: calculated for $\text{C}_7\text{H}_{14}\text{SiN}_2$; C, 54.50; H, 9.15; N, 18.16; observed 54.45, 9.07, 18.07 respectively; i.r. 3200-2900 sb, 1600m, 1570m, 1400s, 1290s, 1255s, 1180s, 1150s, 1050s, 985s, 850sb, 760s, 745s, 650s, 620s cm^{-1} ; ^1H n.m.r. 0.39 δ (8.7H), 2.38 δ (3H) and 6.8 δ (2H).

Dehydration¹⁵⁸ of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: Fine $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (6.0 gm) powder was placed in a flask provided with a ground joint and was covered with SOCl_2 . The mixture was refluxed for several hours. The excess of SOCl_2 which clings to the product (now blue in colour) was removed by repeated evacuation of the flask.

Dehydration¹⁵⁸ of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5.0 gm) was refluxed with 50 ml SOCl_2 . The excess of SOCl_2 was removed by distillation and the residue was dried under vacuum at 40°C .

Preparation¹⁵⁹ of dichlorobis(triphenylphosphine)cobalt (II): Triphenylphosphine (1.5 times the stoichiometric amount i.e. 7.86 gm, 30.0 mmol) was melted in a water bath and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.37 gm, 10.0 mmol) was slowly added to this molten triphenylphosphine with continuous magnetic stirring. The reaction mixture was stirred for 5-10 minutes thereafter, cooled and ground in a mortar. The blue product obtained was treated with hot ethanol for recrystallization [M.pt. 225°C].

Preparation¹⁶⁰ of chlorotris(triphenylphosphine)copper(I): Triphenylphosphine (6.55 gm, 25.0 mmol) was dissolved in 100 ml benzene in which CuCl (0.6015 gm, 6.5 mmol) was added in portions with continuous stirring, and then the reaction mixture was refluxed for Ca. 12 hrs. A shining white microcrystalline mass precipitates out which was isolated after filtration and drying in vacuo. [M.pt. 163°C].

Preparation¹⁶¹ of dichlorotris(triphenylphosphine)ruthenium (III): To a solution of ruthenium trichloride trihydrate (0.2 gm) in methanol (50.0 ml) a six fold excess (1.2 gm) of triphenylphosphine was added with continuous stirring. The solution was stirred for 2 hrs., filtered and the deep brown solution shaken at room temperature under nitrogen for Ca. 2 days. The dark brown crystals of the complex were washed with methanol followed with ether and dried in vacuo at 60°C [M.pt. 135°C].

Preparation of trichlorobis(triphenylarsine)(methanol)-ruthenium(III)¹⁶¹: The hydrated ruthenium trichloride(0.2 gm) and a six fold excess of triphenylarsine(1.5 gm) were reacted in methanol (50.0 ml) with continuous stirring. The reaction mixture was filtered and then refluxed for 3 hrs. by which time green crystals of the complex were started depositing. The crystals were separated through filtration and then repeatedly washed with ether. It was very stable in atmosphere hence dried in air [M.pt.150°C].

PREPARATION OF THE COMPLEXES:

Reaction of N-trimethylsilylimidazole with anhydrous CoCl_2 ; Isolation of chloro(imidazolato)cobalt(II), (I): N-trimethylsilylimidazole(0.416 gm, 2.94 mmol) diluted with 30 ml benzene was added dropwise from a dropping funnel fitted to a round bottomed flask containing CoCl_2 (0.136 gm, 1.05 mmol) suspended in 30 ml benzene, with continuous magnetic stirring at room temperature under dry nitrogen atmosphere. The formation of a light blue oily product was immediately indicated and the reaction mixture was stirred for about 1/2 hr. The mother liquor was decanted off leaving behind the oily mass which was washed several times with pet.-ether and vacuum dried giving microcrystalline solid which melts at 125°C. The crude was dissolved in 50 ml CH_2Cl_2 filtered off to remove impurity, mixed with n-hexane and kept at 5°C for

about two weeks. This gave light blue coloured hexagonal crystals [M.pt. 130°C].

Reaction of N-trimethylsilyl-2-methylimidazole with anhydrous CoCl_2 ; Isolation of chloro(2-methylimidazolato)cobalt (II), (II): It was prepared in the same manner as described earlier for (I) by dropping (0.452 gm, 2.94 mmol) of N-trimethylsilyl-2-methyl-imidazole diluted with 30 ml benzene to a suspension of CoCl_2 (1.36 gm, 1.05 mmol) in 40 ml benzene. The product was separated out of the mother liquor as an oily mass, which on repeated washing with diethyl ether resulted in a microcrystalline solid melting at 90°C . It was recrystallized as for (I) which gave beautiful crystals [M.pt. 102°C].

Reaction of N-trimethylsilylimidazole with $[\text{Co}(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cl}_2$; Isolation of bis(imidazolato)cobalt(II), (III): N-trimethylsilylimidazole (1.28 gm, 9.2 mmol) diluted with 30 ml benzene was added dropwise to a solution of $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (3.00 gm, 4.6 mmol) in 200 ml THF (tetrahydrofuran) with continuous stirring at room temperature under dry nitrogen atmosphere. When whole of the $(\text{CH}_3)_3\text{Si}$ -imidazole had been dropped (30 minutes), the reaction mixture was vigorously stirred for an additional 30 mts. and left standing for 1 hr. The colourless mother liquor was decanted off leaving behind the blue oily mass, which was immediately washed with benzene-THF mixture, then with pet.-ether and the washings

were mixed with the filtrate. The mass was vacuum dried giving light blue coloured amorphous solid [M.pt. 135-145°C]. The filtrate was vacuum dried giving 2.3 gm of a colourless microcrystalline material [M.pt. 79-82°C] which has been identified as $(C_6H_5)_3P$ [Ca. 2.0 mole equivalent of the precursor] from i.r. and elemental analyses. The main product has been recrystallized from CH_2Cl_2/n -hexane giving a microcrystalline solid melting at 147°C.

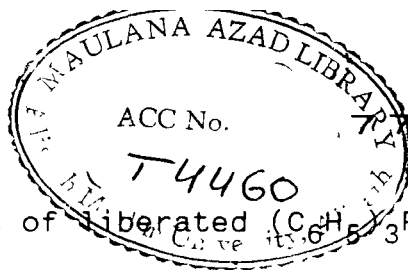
Reaction of N-trimethylsilyl-2-methylimidazole with $[Co\{(C_6H_5)_3P\}_2Cl_2]$, Isolation of bis(2-methylimidazolato)cobalt(II), (IV): Reaction was performed in the same manner as above by taking (0.45 gm, 2.9 mmol) trimethylsilyl-2-methylimidazole in 20 ml benzene and (0.685 gm, 1.05 mmol) $[Co\{(C_6H_5)_3P\}_2Cl_2]$ in 60 ml THF at room temperature. In this case too an oily mass was formed which was washed with ether to result in a solid product. The crude product was recrystallized from CH_2Cl_2/n - hexane giving a blue microcrystalline solid [M.pt. 130°C]. In this case also the filtrate and washings have afforded 0.55 gm (about 2.0 mole-equivalent) of the free $(C_6H_5)_3P$.

Reaction of N-trimethylsilylimidazole with anhydrous $CuCl_2$ affording bis(imidazolato)copper(II), (V): The reagent N-trimethylsilylimidazole (0.7 gm, 5.0 mmol) was dropped to the suspension of the $CuCl_2$ (0.336 gm, 2.5 mmol) in 150 ml THF with continuous stirring. The reaction mixture was further

stirred for Ca. 1 hr. after the reagent has been completely added. It was filtered off to remove the unreacted metal salt impurity and vacuum dried, washed several times with pet.-ether to give amorphous solid. The crude was recrystallized from CH_2Cl_2 / n-hexane [M.pt.180°C].

Reaction of N-trimethylsilyl-2-methylimidazole with CuCl_2 yielding bis(2-methylimidazolato)copper(II), (VI): The reagent N-trimethylsilyl-2-methylimidazole(0.77 gm, 5.0 mmol) was dropped to the suspension of the CuCl_2 (0.336 gm, 2.5 mmol) in 150 ml THF with continuous stirring in the manner as described above. The reaction mixture was further stirred for 1 hr. It was filtered off to remove the unreacted metal salt impurity and vacuum dried, washed several times with pet.-ether to give amorphous solid. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt. 210°C].

Reaction of N-trimethylsilylimidazole with $[\text{Cu}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}]$; Isolation of imidazolato bis(triphenylphosphine)copper(I), (VII): The reagent was treated with equimolar solution of $[\text{Cu}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}]$ in THF with continuous stirring. Immediate curdy white solid formed which slowly redissolved while stirring magnetically at room temperature, under N_2 atmosphere. The reaction mixture was vacuum dried, washed with pet.-ether and again dried in vacuo. The crude was recrystallized from CH_2Cl_2 -n-hexane giving colourless microcrystalline solid [M.pt.185°C]. The washings have



yielded 1.0 mole equivalent amount of liberated $(C_6H_5)_3P$.

Reaction of N-trimethylsilyl-2-methylimidazole with $[Cu\{(C_6H_5)_3P\}_3Cl]$; giving 2-methylimidazolatobis- (triphenyl-phosphine)copper (I), (VIII): The reagent N-trimethyl-silyl-2-methylimidazole was treated with equimolar solution of $[Cu\{(C_6H_5)_3P\}_3Cl]$ in THF as discussed above. Here, too curdy white solid formed which slowly redissolved while stirring at room temperature. The reaction mixture was vacuum dried washed with pet.-ether and dried in vacuo. The crude product was recrystallized from CH_2Cl_2 /n-hexane giving colourless microcrystalline solid, [M.pt. $195^\circ C$]. Here also the washings have yielded 1.0 mole equivalent amount of liberated $(C_6H_5)_3P$.

Preparation of chloro(imidazolato)bis(triphenyl phosphine)-copper(II), (IX): To a suspension of $CuCl_2$ (0.336 gm, 2.5 mmol) in 80 ml THF, solution of $(C_6H_5)_3P$ (1.31 gm, 5.0 mmol) and of the reagent N-trimethylsilylimidazole (0.7 gm, 5.0 mmol) in 50 ml THF both taken in separate dropping funnels were simultaneously dropped with a slow rate with continuous stirring at room temperature. The reaction mixture was stirred for an additional 2 hr., after the whole of the reactants have been added. It was filtered off to remove the impurity of unreacted $CuCl_2$. The mother liquor was vacuum dried and washed with ether. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt. $215^\circ C$].

Preparation of chloro(2-methylimidazolato)bis (triphenylphosphine) copper(II), (X): To a suspension of CuCl_2 (0.336 gm, 2.5 mmol) in 80 ml THF, solution of $(\text{C}_6\text{H}_5)_3\text{P}$ (1.31 gm, 5.0 mmol) and of the reagent N-trimethylsilyl-2-methylimidazole (0.77 gm, 5.0 mmol) both in 50 ml THF were simultaneously dropped as for (IX). The reaction mixture was stirred for an additional 2 hrs. after the whole of the reactants have been dropped in. Filtered off to remove any impurity of unreacted metal salt. The mother liquor was vacuum dried and washed with ether. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt. 185°C].

Reaction of N-trimethylsilylimidazole with anhydrous RuCl_3 ; Isolation of chlorobis(imidazolato)ruthenium (III), (XI): N-trimethylsilylimidazole (2.01 gm, 13.4 mmol) was added dropwise from a dropping funnel to a solution of RuCl_3 (1.0 gm, 4.8 mmol) in 40 ml THF with continuous magnetic stirring under an inert atmosphere of dry N_2 . The dark coloured solution was stirred for one hour which afforded black coloured microcrystalline solid out of the solution. The reaction mixture was further stirred for two hrs. The solid was isolated in the absence of air and moisture as it was moisture sensitive in nature, washed with hexane-ether and dried in vacuo (M.pt. $> 360^\circ\text{C}$).

Reaction of N-trimethylsilyl-2-methylimidazole with anhydrous RuCl_3 ; Isolation of chlorobis(2-methylimidazolato)ruthenium (III), (XII): It was prepared in the same manner as described above for (XI) by dropping (2.06 gm, 13.4 mmol) of the reagent N-trimethylsilyl-2-methylimidazole diluted with 10 ml THF to a solution of RuCl_3 (1.0 gm, 4.8 mmol) in 25 ml THF. The oily mass obtained after removal of solvent in vacuum evaporation was shaken with hexane, finally with ether giving black coloured microcrystalline solid [M.pt. > 360°C].

Reaction of N-trimethylsilylimidazole with $[\text{Ru}(\text{C}_6\text{H}_5)_3\text{As}]_2\text{Cl}_3 \cdot \text{MeOH}$; Isolation of tris(imidazolato)bis(triphenylarsine)ruthenium(III), (XIII): Reagent N-trimethylsilylimidazole (0.48 gm, 0.6 mmol) was added dropwise to a continuously stirring solution of $[\text{Ru}((\text{C}_6\text{H}_5)_3\text{As})_2\text{Cl}_3 \cdot \text{MeOH}]$ (0.175 gm, 0.2 mmol) in 20 ml THF. The colour of the solution was brown which further intensified on addition of the reagent. Microcrystalline solid separated out of the solution while stirring which was continued for Ca. 2 hrs. The mother liquor was kept overnight at low temperature for further recrystallization. The solid was separated through filtration in closed system. As the mother liquor still had some brown colour so it was mixed with hexane and kept at 5°C for two days giving the next crop of the compounds. [M.pt. > 360°C].

Reaction of N-trimethylsilyl-2-methylimidazole with $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}_2\text{Cl}_3 \cdot \text{MeOH}]$; Isolation of tris(2-methylimidazolato) bis(triphenylarsine)ruthenium(III), (XIV): The isolation of the product tris(2-methylimidazolato)bis(triphenylarsine)ruthenium(III) was performed in the same manner as described above for (XIII) by treating the reagent N-trimethylsilyl-2-methylimidazole (0.096 gm, 0.6 mmol) diluted in 10 ml THF to a continuously stirring solution of the precursor (0.175 gm, 0.2 mmol) in 20 ml THF. The microcrystalline solid which gradually appeared in the solution was filtered off and dried in vacuo. The mother liquor when treated with n-hexane and kept at 5°C gave the microcrystalline solid. It was washed with ether and dried in vacuo. [M.pt. > 360°C].

Reaction of N-trimethylsilylimidazole with $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}_2]$; Isolation of bis(imidazolato)bis(triphenylphosphine)ruthenium(II), (XV): N-trimethylsilylimidazole (0.051 gm, 0.36 mmol) was added dropwise from a dropping funnel to a solution of $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}_2]$ (0.176 gm, 0.18 mmol) dissolved in THF under dry N_2 atmosphere. The initial brown colouration of the solution got intensified on the addition of the reagent. It was magnetically stirred for additional 2 hrs. Dark brown microcrystalline solid appeared in the solution. It was kept at low temperature for several hours to effect further crystallization of the product. All

manipulations were done strictly in the atmosphere of dry N_2 to avoid oxidation of Ru(II). The brown solid was decanted off from the mother liquor and washed several times with ether and dried in vacuo [M.pt. $218^{\circ}C$]. The washings were collected and dried in vacuo which yielded (Ca. 0.05 gm) microcrystalline solid. It was identified as $(C_6H_5)_3P$ from the melting point [M.pt. $80^{\circ}C$], i.r. and microanalyses of the compound. The liberated triphenyl-phosphine was apparently equivalent to one mole equivalent with respect to the precursor taken for the reaction.

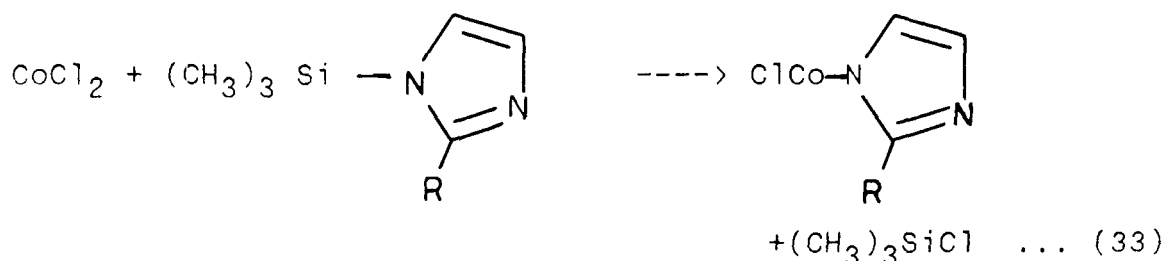
Reaction of N-trimethylsilyl-2-methylimidazole with $[Ru\{(C_6H_5)_3P\}_3Cl_2]$ Isolation of bis(2-methylimidazolato) bis(triphenylphosphine)ruthenium (II), (XVI): The reagent N-trimethylsilyl-2-methylimidazole (0.055 gm, 0.36 mmol) was treated with $[Ru\{(C_6H_5)_3P\}_3Cl_2]$ (0.176 gm, 0.18 mmol) in the same manner as has been described for the above reaction. Here too, the washings when dried in vacuo have provided white crystalline powder identified as $(C_6H_5)_3P$ from melting point, microanalyses and spectroscopic data. The liberated $(C_6H_5)_3P$ has been equivalent to 1.0 mole equivalent with respect to the starting precursor.

The brown coloured main product was dried in vacuum [M.pt. $230^{\circ}C$].

RESULTS AND DISCUSSION

The observed reactivity of N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole towards transition metal chlorides and their complexes is reasonably the consequence of the affinity of $-(\text{CH}_3)_3\text{Si}$ group of the reagents for the chlorine atom in the substrates, effecting the release of $(\text{CH}_3)_3\text{SiCl}$. The results of the elemental analyses, stoichiometries and the experimentally determined molecular weight of the final products of the various reactions have been shown in Table-I and II.

Formation of chloro(imidazolato)cobalt(II), (I); chloro(2-methylimidazolato)cobalt(II), (II); bis(imidazolato) cobalt (II), (III) and bis(2-methylimidazolato)cobalt(II), (IV): For the reactions of CoCl_2 with trimethylsilylimidazole and trimethylsilyl-2-methylimidazole, the final product in each case has been characterized as $[\text{CoLCl}]$ (L=imidazolate or 2-methylimidazolate) even though the silyl reagents were taken in excess from that required for the total removal of chlorine as $(\text{CH}_3)_3\text{SiCl}$, i.e.



R= H, (I)

R= CH_3 , (II)

There is no indication of the formation of even traces of metallic cobalt in either of the reactions, unlike to that reported¹⁶² for the reaction of $\text{LiN}(\text{C}_2\text{H}_5)_2$ with CoCl_2 , ruling out the possible reduction of metal salt in the present case.

Reaction of the precursor $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with the reagents is interesting in that the final product in both the cases does not contain coordinated $(\text{C}_6\text{H}_5)_3\text{P}$ rather an equivalent amount of it has been liberated out as free $(\text{C}_6\text{H}_5)_3\text{P}$ (experimental section) yielding bis(imidazolato)-cobalt(II), (III) and bis(2-methylimidazolato)cobalt(II), (IV). Assuming imidazolate moiety as 4 electron donor (behaving as σ as well as π donor) similar to that indicated¹⁶³ for amido moiety in transition metal amides, the electron count suggests that the cobalt ion in (III) and (IV) attains a share of 15 electrons suggesting that (III) and (IV) are electron deficient species. It is surprising that $(\text{C}_6\text{H}_5)_3\text{P}$, a well known stabilizing ligand owing to its strong π -acceptor property, is being totally liberated out from coordination to metal ion though the latter is electronically not satisfied in view of 18 electron rule. This fact has been further substantiated by the observation that the attempt to obtain $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_n\text{L}_2]$ ($n=1$ or 2) by reacting (III) and (IV) with appropriate amount of $(\text{C}_6\text{H}_5)_3\text{P}$ in tetrahydrofuran leads to the isolation of

unreacted starting materials. The analogous compound bis-(hexamethyldisilyldiamino)cobalt(II), $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$, prepared by Bürger et al.¹⁶⁴ also did not show complex forming ability even with a strong σ donor. However, the reaction of $\text{LiN}\{(\text{CH}_3)_3\text{Si}\}_2$ with $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ is reported¹⁶⁵ to yield three coordinate complex $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{N}\{(\text{CH}_3)_3\text{Si}\}_2]_2$ in which the metal ion has acquired a share of 17 electrons with one mole of $(\text{C}_6\text{H}_5)_3\text{P}$ retained and the π -acceptor properties of $(\text{C}_6\text{H}_5)_3\text{P}$ is supposed to play an important role for its stabilization.

These complexes are sensitive to air, turning to dark blue sticky liquids and are readily solvolysed by water and alcohol forming pink solutions (with decomposition). They are fairly soluble in CH_2Cl_2 and THF.

Formation of bis(imidazolato)copper(II), (V); bis(2-methylimidazolato)copper(II), (VI); (imidazolato)bis(triphenylphosphine)copper(I), (VII); (2-methylimidazolato)bis(triphenylphosphine)copper(I), (VIII); chloro(imidazolato)bis(triphenylphosphine)copper(II), (IX) and chloro(2-methylimidazolato)bis(triphenylphosphine)copper(II), (X): For the reactions of anhydrous CuCl_2 with N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole the product in each case has been identified as $[\text{CuL}_2]$, suggesting the replacement of both the chlorines by imidazolate moieties as shown below:

The reaction of CuCl_2 with $(\text{C}_6\text{H}_5)_3\text{P}$ is known¹⁶⁶ to yield invariably a Cu(I) complex. However, in the present reaction condition, it has been performed in the presence of the reagent *N*-trimethylsilylimidazole or *N*-trimethylsilyl-2-methylimidazole. The final product in either case has the stoichiometry $[\text{Cu}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{LCI}]$; (IX) or (X). The physico-chemical investigations on the complexes vide infra agree with a d^9 configuration of copper i.e. with +2 oxidation state confirming that the complexes (IX) and (X) are the genuine Cu(II) species, suggesting that the imidazolate moiety protects the reduction of metal ion presumably due to its strong π -donating capability. These complexes are soluble in most of the organic solvents, moisture sensitive and get solvolysed in water.

The compounds have been characterized using various physico-chemical methods. The analytical data (Table-I and II) are in agreement with the proposed stoichiometries of the compounds. The experimentally determined molecular weights (Table-II) suggest their monomeric nature in the solution. The important characteristic imidazolate and $(\text{C}_6\text{H}_5)_3\text{P}$ ring vibrations as well as $\nu(\text{M-N})$, $\nu(\text{M-P})$ and $\nu(\text{M-Cl})$ stretching vibrations manifested in the i.r. spectra of the various complexes have been summarized in Table-III and IV. The characteristic imidazole ring vibrations are slightly shifted $(10-20) \text{ cm}^{-1}$ from their positions in the

free imidazole, similar to those observed^{42,89-94} in the spectra of transition metal complexes of neutral imidazole as well as of the imidazolyl borate anion $[\text{BH}_{4-n}\text{Iz}_n]^-$. It can be seen from Table-IV that some of the characteristic bands of the imidazolate ring vibrations overlap with that characteristic of the $(\text{C}_6\text{H}_5)_3\text{P}$, nevertheless, bands which are diagnostic for the presence of imidazolate and/or $(\text{C}_6\text{H}_5)_3\text{P}$ in the compounds are clearly indicated^{42,138}. A band at about 390 cm^{-1} is attributed to $\nu(\text{M-N})$ [cf. $\nu(\text{M-N})$ in imidazole complexes appears⁴² at Ca. 250 cm^{-1}]. In $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\text{M}=\text{Co}, \text{Zn}, \text{Cd}, \text{Hg}$) too $\nu(\text{M-N})$ occurs at Ca. 390 cm^{-1} , which has been attributed^{153,164,167} to the additional π -donor nature of the ligand. The same may be true in the present complexes. The i.r. data therefore substantiates that the imidazolate moiety in the present complexes, acts as a four electron donor (σ and π). The band of medium intensity at about 320 cm^{-1} arising in (I) and (II) is assigned¹³⁵ to $\nu(\text{M-Cl})$ stretching vibrations. For the compounds (VII)-(X) the $\nu(\text{M-Cl})$ vibrations are indicated at the appropriate positions^{135,138} (Table-IV).

The results of the electronic spectra and magnetic susceptibility measurements are summarized in Table-V and VI. The electronic spectra recorded in non-polar solvents are nearly identical to the reflectance spectra of the solids, indicating the existence of similar species in solution as well as in solids. The bands observed in CH_2Cl_2 for (I)-(IV)

are reasonably assigned to the transitions characteristic of a linear arrangement¹⁶⁸ of ligand around cobalt(II) in $D_{\infty h}$ symmetry similar to that reported¹⁶⁹ for gaseous CoCl_2 . The electronic spectra in THF are, however different containing a band at $15,000 \text{ cm}^{-1}$ with a shoulder at Ca. $17,000 \text{ cm}^{-1}$ attributable to d-d transitions in a tetrahedral geometry¹⁷⁰ around cobalt(II) ion. This change from linear in the solid and in CH_2Cl_2 solution to tetrahedral in THF solution may be due to coordination of THF in solution which does not seem uncommon in view of a strong donor capacity of THF¹⁶³.

Solutions of (I), (II), (III) and (IV) in methanol and ethanol give the characteristic pink colour of the hexa aquo-complex and their visible spectra are consistent with an octahedral geometry¹⁷¹ for the solvolysed product.

The observed magnetic moment values for (I)-(IV) (Table-V) are consistent with a high spin d^7 system¹⁷². As has been suggested earlier^{164,168,169} the ligand field by two nitrogens in a linear arrangements would not be large enough to allow the mixing of non degenerate excited states, resulting in a higher μ_{eff} from that of the theoretical spin-only value.

The broad band appearing at Ca. $14,000 \text{ cm}^{-1}$ in the ligand field spectrum of bis(imidazolato)copper(II), (V) and

bis(2-methylimidazolato)copper(II), (VI) is assignable to the envelope of transitions $^2A_{1g}$, $^2B_{2g}$, $^2E_g \leftarrow ^2B_{1g}$ characteristic of square-planar geometry¹⁷³. The observed μ_{eff} value of 1.9 B.M. is consistent with a d^9 configuration of copper ion.

The μ_{eff} values for (IX) and (X) are somewhat higher from the calculated spin-only ($S=1/2$), as expected owing to the spin-orbit coupling contribution, however, the magnitude lies in the range normally observed for various copper(II) complexes¹⁷⁴. The electronic spectra show a weak broad band at Ca. $22,000 \text{ cm}^{-1}$, however, for regular tetrahedral copper(II) complexes the region $10,000\text{--}20,000 \text{ cm}^{-1}$ is reported¹⁷⁵ to be blank. As there is no band in the $14,000\text{--}16,000 \text{ cm}^{-1}$ region characteristic of square-planar geometry and hence it may be deduced that the compound acquires a distorted tetrahedral array of ligand around Cu(II) ion. The main d-d band expected in the near i.r. region could not be recorded as it occurs beyond the range of our instrument. A regular tetrahedral geometry in view of the well known reasons^{174,176} is unjustified rather a flattening¹⁷⁶ from regular tetrahedral geometry do occur in some cases. In the present complexes (IX) and (X) presumably the steric factor is predominating for adopting preferentially a tetrahedral structure^{174,177}. The present data rule out any possibility for the formation of a reduced Cu(I) species (cf. reaction of CuCl_2 with $(\text{C}_6\text{H}_5)_3\text{P}$ invariably yields¹⁶⁶ a copper (I)

complex). Furthermore, the products do contain one chlorine vide supra, even though the reagents were sufficient to cause the replacement of both the chlorines. Steric factor is presumably operative in restricting the further substitution. The same argument seems valid to account for the release of $(C_6H_5)_3P$ from the reaction of $[Cu\{(C_6H_5)_3P\}_3Cl]$ with the reagents corroborating the reaction given by equation (35). In the absence of any spectral and magnetic data it can however, be assumed, in view of the analogy for the Cu(II) complex that (VII) and (VIII) also attain a tetrahedral structure.

Formation of chlorobis(imidazolato)ruthenium(III), (XI); Chlorobis(2-methylimidazolato)ruthenium(III), (XII): The reaction of N-trimethylsilylimidazole/N-trimethylsilyl-2-methylimidazole towards anhydrous $RuCl_3$ suspended in THF was apparently slow yielding a dark coloured hygroscopic solid which could not be recrystallized owing to its insolubility in normal non-polar organic solvents. It was soluble in methanol and tetrahydrofuran suggesting its oligomeric or polymeric nature. The results of elemental analyses for both the cases confirm the stoichiometry as $[RuL_2Cl]_x$ (L=imidazolate or 2-methylimidazolate). The presence of one chlorine in the molecular unit suggest that like $CoCl_2$ reaction with the reagents one chlorine is always retained

even though an excess of the reagent has been used to effect the total release of chlorine as $(\text{CH}_3)_3\text{SiCl}$. The electron counts in this case indicates that Ru(III) acquires a total of $15e^-$ in its shell. It is apparently an electron deficient as well as coordinatively unsatisfied and therefore prone to polymerization. The electrical conductivity measurements in DMSO indicate the non-electrolytic nature of the complexes. The nature of bonding and structure of the compound have been ascertained using magnetic susceptibility measurements and spectroscopic studies. Infra-red spectrum of the complex shows the characteristic ring vibrations R_1 , R_2 , R_3 , R_4 of the coordinated imidazolate moiety at the expected^{42,89-94} positions [Table-VII]. The appearance of a doublet of medium intensity at 460 and 480 cm^{-1} is assignable to the $\nu(\text{Ru}-\text{N})$ stretching vibration [Cf. Ru-N generally appears at 463 cm^{-1} in Ru (III) complexes¹⁷⁸]. The resonance coupling¹⁷⁹ in the crystal lattice may be the cause of splitting of this band. The i.r. spectrum did not contain a band in 250-300 cm^{-1} region attributable to terminal $\nu(\text{Ru}-\text{Cl})$ vibration suggesting that the complex probably involves chlorine bridged polymerization. However, the bridging $\nu(\text{Ru}-\text{Cl})$ vibration is reported¹³⁵ to occur below 250 cm^{-1} which fall below the range of our instrument and hence could not be ascertained. However existence of ligand bridging through imidazolate nitrogens may also be a potential viability,

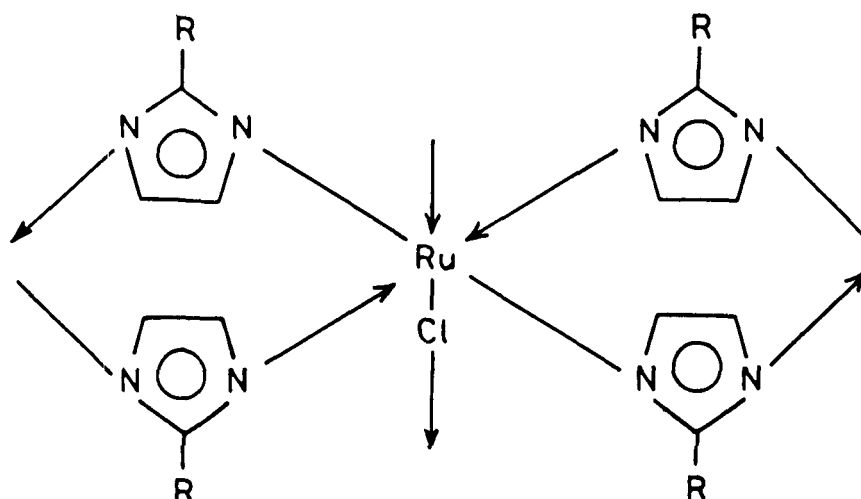
which has been reported¹⁸⁰ to be present in a number of bi- and tri- nuclear imidazolate complexes with transition metal ions.

The observed magnetic moment value of 1.60 B.M. for (XI) and 1.80 B.M. for (XII) (Table-VIII) is considerably lower from that theoretically expected for spin-only value of d^5 system. This lowering in the observed μ_{eff} value in some of the ruthenium (III) complexes by the previous workers has been interpreted in terms of the existence of the low symmetry ligand field in the complex molecule¹⁸¹. The present complexes (XI) and (XII) are polymeric in nature which may be involving chlorine as well as imidazolate bridging and therefore the possibility of the existence of anti-ferromagnetic interaction could not be ruled out. The antiferromagnetic interaction is reported¹⁸² to be pronounced in presence of chlorine and or ligand bridging in the complex molecule.

The electronic spectrum of the complexes (XI) and (XII) exhibited three well defined absorptions at 370 ($27,027 \text{ cm}^{-1}$), 430 ($23,255 \text{ cm}^{-1}$) and 620 nm ($16,129 \text{ cm}^{-1}$). These bands can be assigned to those arising from ligand to metal charge-transfer bands as well as d-d transitions. It is well known⁶⁹ that the imidazole ring itself does not show

absorption bands above 240 nm. The U.V. visible spectrum of RuCl_3 in LiCl-KCl eutectic melt is reported¹⁸³ to exhibit a number of bands between 33,000 to 8,420 cm^{-1} range which have been expressed in terms of ligand to metal charge-transfer excitation as well as those arising from spin forbidden as well as spin allowed d-d transitions from the $^2\text{T}_{2g}$ ground state of the metal ion. However, the complex $[\text{Ru}(\text{NH}_3)_5(\text{IzH})_3]^+$ is reported⁶⁹ to exhibit two bands at 360 and 550 n.m., the latter one is suggested to be characteristic of ligand to metal charge-transfer excitation.

In the electronic spectrum of the present complexes $[\text{RuClL}_2]_x$ (L = imidazolate (XI); 2-methylimidazolate (XII)) the band observed at 27,027 with an extinction coefficient of $\epsilon = 2600$ is reasonably due to ligand (π) to metal ($d\pi$ orbital) charge-transfer. The position of this ligand to metal charge-transfer band is at comparatively lower energy from that reported¹⁸³ in RuCl_3 , itself, which may be ascribed to the π -donor nature of the imidazolate moiety. The bands at 23,255 and 16,129 cm^{-1} are assignable (Table-VIII) to spin allowed transitions $^2\text{T}_{1g}$, $^2\text{A}_{1g} \leftarrow ^2\text{T}_{2g}$ and $^2\text{T}_{2g}$, $^2\text{E}_g \leftarrow ^2\text{T}_{2g}$ respectively. The imidazolate and or chlorine bridged octahedral polymeric structure as shown in figure (XXI) seems plausible in view of the present investigations.



R = H for (XI)

R = CH₃ for (XII)

(Figure-XXI)

Formation of tris(imidazolato)bis(triphenylarsine)ruthenium (III), (XIII) and tris(2-methylimidazolato)bis(triphenylarsine)ruthenium(III), (XIV): The product of the reaction of $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}_2\text{Cl}_3 \cdot \text{MeOH}]$ with the reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole, in each case, has been identified as $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}_2\text{L}_3]$ [L=imidazolate (XIII) and 2-methylimidazolate (XIV)] as is evident from analytical (Table- VI) and physico-chemical data (Table-VII and VIII). Here all the three chlorines of the precursor have been substituted by the imidazolate or 2-methylimidazolate moiety.

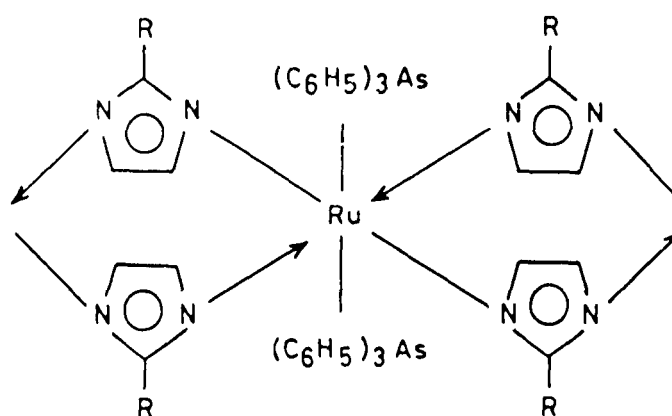
The characteristic bands of the coordinated MeOH usually indicated¹⁶¹ as a strong band at 1000 cm^{-1} with some

weak intensity bands in $3500\text{--}3450\text{ cm}^{-1}$ are absent in the i.r. spectrum of the products (XIII) and (XIV) ruling out their possible inclusion in crystal lattice of these compounds. The bands for imidazolate ring vibrations and coordinated triphenylarsine (Table - VIII) are located at the appropriate^{42,89-94} positions. The ν (Ru-N) stretching vibration in (XIII) and (XIV) appear at Ca. 480 cm^{-1} and the weak band that arise at around 330 cm^{-1} may be characteristic¹³⁸ of ν (M-As).

The magnetic moment value of 2.18 B.M. for (XIII) and 2.23 B.M. for (XIV) is in the range reported¹⁸¹ for octahedral Ru(III) complexes with $^2T_{2g}$ ground state. Their electronic spectra recorded in DMSO exhibited five absorption maxima centered at 330 ($30,303\text{ cm}^{-1}$), 424 ($23,584\text{ cm}^{-1}$), 592 ($16,891\text{ cm}^{-1}$), 710 ($14,084\text{ cm}^{-1}$) and 770 nm ($12,987\text{ cm}^{-1}$) which are assignable^{181,183} to ligand (π) \rightarrow metal ($d\pi$) charge-transfer excitation as well as arising from spin allowed and spin forbidden d-d transitions from $^2T_{2g}$ ground state. It can be seen that ligand to metal-charge transfer transition depends only on the energy of the donor ligand molecular orbital, as the t_{2g} orbital of the metal should essentially be non-bonding in the ground state. Considerable mixing between the $d\pi$ orbital on the metal and the π -system of the ligand may occur similar to that has

been shown for a number of ruthenium(II) pyridine complexes¹⁸⁴.

This assumption seems meaningful in the present ruthenium(III) imidazolate complexes too. The mixing of ligand and metal π orbitals has an important effect on the energy of the ligand to metal charge-transfer. Deprotonation of the series of the xanthine ligand is shown⁷⁰ to cause the purine π -donor level to shift the energy of the charge transfer band to $18,181\text{ cm}^{-1}$. This shift is much higher in energy in the present complexes [cf. 27,027 for (XI), and 30,303 for (XIII)] which may be attributed to an enhanced stabilization of the π -system in the imidazolate moiety relative to the imidazole itself. The observed bands at higher wavelength (lower in energy) (Table-VIII) are reasonably assigned to spin allowed and spin forbidden d-d transitions characteristic of octahedral environment around Ru(III) ion as is shown in figure (XXII).

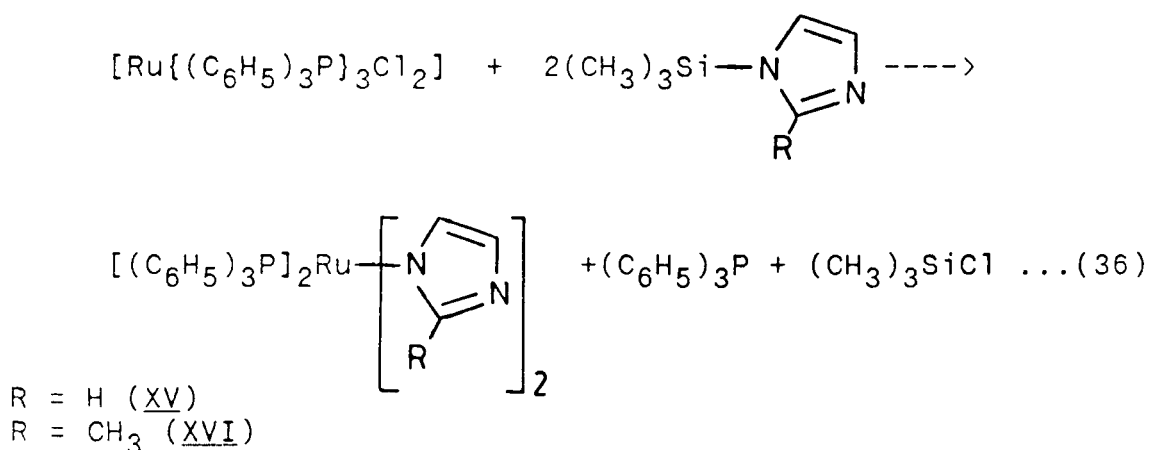


R = H (XIII)

R = CH₃ (XIV)

(Figure XXII)

Formation of bis(imidazolato)bis(triphenylphosphine)ruthenium(III), (XV) and bis(2-methylimidazolato)bis(triphenylphosphine)ruthenium(II), (XVI): The analytical data (Table-VI) of the product obtained from the reaction of $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Cl}_2]$ with the reagents N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole suggest the stoichiometry of the product as $[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{L}_2]$ (L=imidazolate, (XV) or 2-methylimidazolate, (XVI)). The reaction may be typified as represented by the following equation:



In this reaction too, both the chlorines are being released as $(\text{CH}_3)_3\text{SiCl}$ accompanied with the liberation of one mole equivalent of free $(\text{C}_6\text{H}_5)_3\text{P}$ [Please see experimental part]. The mode of reaction is apparently different from that has been recorded for $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ where all the coordinated $(\text{C}_6\text{H}_5)_3\text{P}$ are liberated as free $(\text{C}_6\text{H}_5)_3\text{P}$ (vide supra) during the course of the reaction giving the stoichiometry as $[\text{CoL}_2]$. The electron count in the complex suggests that Ru(II) in the complex (XV) and (XVI) has

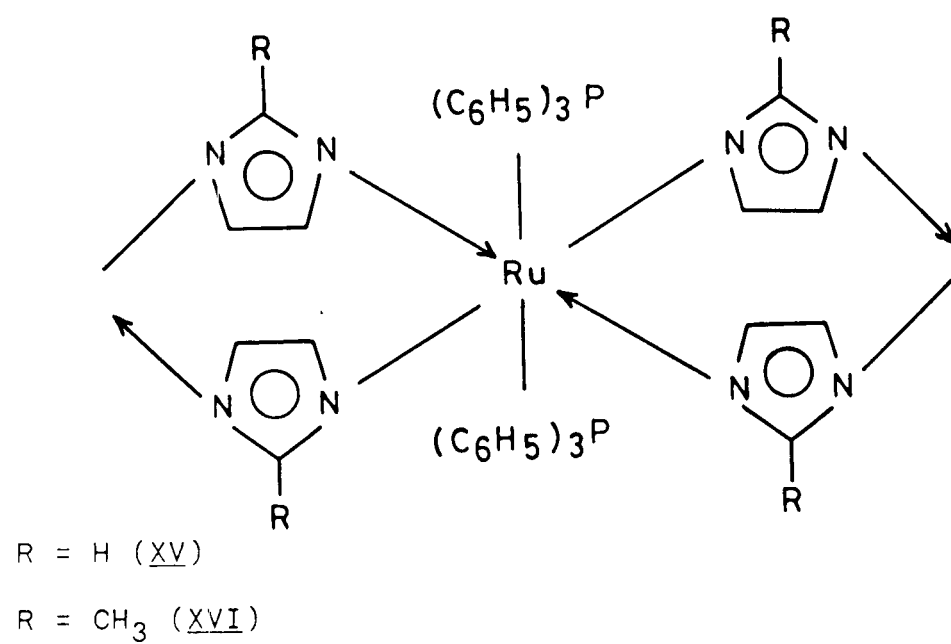
attained a stable configuration of $18 e^-$ in its shell. This reflects that $(C_6H_5)_3P$ has more pronounced π -acidity for Ru(II) relative to Co(II).

The i.r. spectra of the compounds contain bands characteristic of the imidazolate^{42,89-94} ring vibrations as well as those arising from coordinated triphenylphosphine^{127,185}. The metal-ligand vibrations have been ascertained from the study of the spectra in the far i.r. region, which shows bands at 400 and 320 cm^{-1} assignable to $\nu(M-N)$ ¹⁷⁸ and $\nu(M-P)$ ¹³⁸ stretching vibrations respectively.

The observed diamagnetism of the compounds (XV) and (XVI) confirms a high spin d^6 configuration of the metal ion with +2 oxidation state of ruthenium in an octahedral environment of the ligand.

The reflectance spectrum of the complex shows only one broad band at $16,129\text{ cm}^{-1}$ which can be assigned to those arising from metal $d(\pi)$ to ligand π^* charge-transfer excitation. This charge - transfer transition appears at lower energy in the present complexes from that reported⁷⁰ for the Ru(II)-amine complexes.

In view of the above observations an octahedral arrangement of ligand is proposed around Ru(II) ion as is shown in figure (XXIII).



(Figure XXIII)

TABLE-I
Analytical data of the compounds

Complexes	% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% M Found (Calcd.)	% Cl Found (Calcd.)	Mol. Wt. Found (Calcd.)
[Co(Iz)Cl] (I)	22.2 (22.3)	1.6 (1.9)	17.3 (17.4)	36.0 (36.5)	20.8 (22.0)	172 (161)
[Co(MeIz)Cl] (II)	27.8 (27.4)	2.5 (2.9)	15.4 (16.0)	32.7 (33.6)	20.0 (20.2)	191 (175)
[Co(Iz) ₂] (III)	28.5 (28.6)	2.4 (2.4)	22.1 (22.2)	45.4 (46.8)	-	208 (193)
[Co(MeIz) ₂] (IV)	34.2 (34.3)	3.3 (3.6)	19.9 (20.0)	41.8 (42.1)	-	233 (220)

TABLE-II
Analytical data of the complexes

Complexes		% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% M Found (Calcd.)	% Cl Found (Calcd.)	Mol. Wt. Found (Calcd.)
[Cu(Iz) ₂]	(V)	36.1 (36.5)	3.0 (3.0)	27.8 (28.3)	30.9 (32.2)	-	205 (198)
[Cu(MeIz) ₂]	(VI)	42.0 (42.6)	3.9 (4.4)	24.2 (24.8)	27.0 (28.2)	-	235 (226)
[Cu{(C ₆ H ₅) ₃ P} ₂ (Iz)]	(VII)	70.9 (71.5)	4.9 (5.0)	4.0 (4.3)	8.4 (9.7)	-	635 (655)
[Cu{(C ₆ H ₅) ₃ P} ₂ (MeIz)]	(VIII)	70.8 (71.8)	5.0 (5.2)	4.1 (4.2)	8.5 (9.5)	-	650 (669)
[Cu{(C ₆ H ₅) ₃ P} ₂ (Iz)Cl]	(IX)	67.3 (67.8)	4.7 (4.8)	3.9 (4.1)	7.8 (9.2)	4.7 (5.2)	678 (690)
[Cu{(C ₆ H ₅) ₃ P} ₂ (MeIz)Cl]	(XL)	68.0 (68.2)	4.9 (5.0)	3.7 (4.0)	8.1 (9.0)	4.2 (5.0)	715 (704)

TABLE-III

Imidazolate - ring, M-N and M-Cl bond stretching frequencies (Cm^{-1})
observed in the i.r. spectra of the compounds.

Complexes	Imidazolate Ring Vibrations				$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
		R ₁	R ₂	R ₃	R ₄	
[Co(Iz)Cl]	(<u>I</u>)	1545s	1480m	1420s	1345m	385s 325m
[Co(MeIz)Cl]	(<u>II</u>)	1565s	1480m	1420s	1330m	390s 320m
[Co(Iz) ₂]	(<u>III</u>)	1555s	475m	1425s	1350m	385s -
[Co(MeIz) ₂]	(<u>IV</u>)	1540s	1490m	1420s	1335s	375s -

TABLE-IV

Imidazolate and $(C_6H_5)_3P$ -ring, M-N, M-P and M-Cl bond stretching frequencies (cm^{-1}) observed in the i.r. spectra of the complexes.

Complexes	Imidazolate-ring				$(C_6H_5)_3P$ -ring	$\nu(M-N)$	$\nu(M-Cl)$	$\nu(M-P)$
	R ₁	R ₂	R ₃	R ₄				
$[Cu(Iz)_2]$	(V)	1555s, 1475m, 1430s, 1320s;			-	375s	-	-
$[Cu(MeIz)_2]$	(VI)	1550s, 1480m, 1420s, 1340m;			-	375s	-	-
$[Cu((C_6H_5)_3P)_2(Iz)]$	(VII)	1550s, 1480s, 1430s, 1320m;			1480s, 1430s, 1090s, 740s, 720s, 510s,	370m, 490s	-	320w
$[Cu((C_6H_5)_3P)_2(MeIz)]$	(VIII)	1555s, 1475s, 1430s, 1345m;			1475s, 1430s, 1100s, 750s, 720s, 510s, 490s	380m	-	310w
$[Cu((C_6H_5)_3P)_2(Iz)Cl]$	(IX)	1530s, 1480s, 1420s, 1320m;			1480s, 1420s, 1090s, 740s, 700s, 510s, 490s	370m, 270m	270m	330w
$[Cu((C_6H_5)_3P)_2(MeIz)Cl]$	(X)	1550s, 1475s, 1430s, 1350m;			1475s, 1430s, 1090s, 740s, 700s, 510s, 490s	375m, 270m	270m	310w

TABLE-V

μ_{eff} (B.M.)^{*} and ligand field bands (cm^{-1}) observed in the electronic spectra of solid and solutions of the complexes and their assignments.

Complexes	μ_{eff} (B.M.)	Band Position (cm^{-1})	Assignment
[Co(Iz)Cl]	(I)	40,800 , 30,300	c.t.
		(40,200 , 31,260)	
		23,220 (22,410)	$4\pi_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
		16,600 (16,000)	$4\bar{\epsilon}_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
[Co(MeIz)Cl]	(II)	11,500 (11,980)	$4\Delta_g(F) \leftarrow 4\bar{\epsilon}_g(F)$
		40,520 , 30,780	c.t.
		(41,120 , 32,260)	
		23,300 , 22,500	$4\pi_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
[Co(Iz) ₂]	(III)	16,670 (16,130)	$4\bar{\epsilon}_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
		11,360 (12,310)	$4\Delta_g(F) \leftarrow 4\bar{\epsilon}_g(F)$
		40,550 , 30,280	c.t.
		(41,270 , 32,260)	
		23,200 (22,500)	$4\pi_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
		16,550 (16,250)	$4\bar{\epsilon}_g(P) \leftarrow 4\bar{\epsilon}_g(F)$
		11,360 (11,790)	$4\Delta_g(P) \leftarrow 4\bar{\epsilon}_g(F)$

Table-V Contd...

Complexes	μ_{eff} (B.M.)	Band Position (cm^{-1})	Assignment
[Co(MeIz) ₂]	4.60	40,500 , 30,800 (41,030 , 30,800)	c.t.
		23,480 (23,200)	$4\pi_g(P) \leftarrow \bar{4}\bar{\Sigma}_g(F)$
		16,800 (15,750)	$4\bar{\Sigma}_g(P) \leftarrow \bar{4}\bar{\Sigma}_g(F)$
		11,560 (11,790)	$4\Delta_g(P) \leftarrow \bar{4}\bar{\Sigma}_g(F)$
[Cu(Iz) ₂]	1.86	14,500 (14,300)	$2A_{1g}, 2B_{2g}, 2E_g \leftarrow \bar{2}B_{1g}$
[Cu(MeIz) ₂]	1.91	14,260 (14,100)	$2A_{1g}, 2B_{2g}, 2E_g \leftarrow \bar{2}B_{1g}$
[Cu[(C ₆ H ₅) ₃ P] ₂ Iz]Cl]	1.93	22,700 (22,200)	Blank
[Cu[(C ₆ H ₅) ₃ P] ₂ MeIz]Cl]	1.91	22,000 (21,700)	-do-

Positions in CH₂Cl₂ solution given in parentheses, * Non SI unit employed
B.M. = $0.9274 \times 10^{-23} \text{ JT}^{-1}$.

TABLE-VI

Analytical data of the complexes.

Complexes	% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% M Found (Calcd.)	% Cl Found (Calcd.)
$[\text{Ru}(\text{Iz})_2\text{Cl}]_x$ (XI)	26.4 (26.6)	2.2 (2.20)	20.5 (20.7)	37.0 (37.4)	12.4 (13.12)
$[\text{Ru}(\text{MeIz})_2\text{Cl}]_x$ (XII)	31.8 (32.2)	3.2 (3.3)	18.7 (18.8)	33.1 (33.9)	10.9 (11.9)
$[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}(\text{Iz})_3]$ (XIII)	59.0 (59.1)	4.3 (4.3)	9.2 (9.2)	10.7 (11.1)	-
$[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{As}\}_2(\text{MeIz})_3]$ (XIV)	60.2 (60.3)	4.6 (4.7)	8.7 (8.8)	10.1 (10.5)	-
$[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{Iz})_2]$ (XV)	66.1 (66.3)	4.6 (4.7)	7.3 (7.4)	13.1 (13.3)	-
$[\text{Ru}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{MeIz})_2]$ (XVI)	66.8 (67.1)	5.0 (5.1)	7.0 (7.1)	12.4 (12.8)	-

TABLE-VII

Imidazolate and $(C_6H_5)_3P/(C_6H_5)_3As$ - ring, M-N, M-Cl and M-P/As bond stretching frequencies (Cm^{-1}) observed in the i.r. spectra of complexes.

Complexes	Imidazolate ring vibration				$(C_6H_5)_3P/(C_6H_5)_3As$	$\nu(M-N)$	$\nu(M-P)$
	R_1	R_2	R_3	R_4			
$[Ru(Iz)_2Cl]_x$ (XI)	1535s	1490s	1425s	1325s	-	460,480d	-
$[Ru(MeIz)_2Cl]_x$ (XII)	1550s	1485s	1425s	1330m	-	465,480d	-
$[Ru\{(C_6H_5)_3As\}_2(Iz)_3]$ (XIII)	1550s	1480s	1435s	1330s	1480s, 1435s, 1100s, 740s, 510s, 500m	480m	330w
$[Ru\{(C_6H_5)_3As\}_2(MeIz)_3]$ (XIV)	1550s	1485s	1430m	1325m	1485s, 1430m, 1090s, 690s, 510s, 490s	480m	325w
$[Ru\{(C_6H_5)_3P\}_2(Iz)_2]$ (XV)	1540s	1475m	1440s	1325m	1475s, 1440s, 1090s, 690s, 510s, 500s	400m	320w
$[Ru\{(C_6H_5)_3P\}_2(MeIz)_2]$ (XVI)	1540s	1480m	1430s	1320s	1480m, 1430s, 1100s, 700s, 510s, 500m	400m	320w

TABLE-VIII

μ_{eff} (B.M.)* and ligand field bands (cm^{-1}) observed in the electronic spectra of the complexes and their assignments.

Complexes	μ_{eff} (B.M.)	Band Position (cm^{-1})	Extinction Coefficient (E)	Assignment
[Ru(Iz) ₂ Cl] _x	(XI)	27,027	2600	c.t.
		23,255		$2T_{1g}$, $2A_{1g}$ <--- $2T_{2g}$
		16,129		$2T_{2g}$, $2E_g$ <--- $2T_{2g}$
[Ru(MeIz) ₂ C ⁺]	(XII)	27,110		c.t.
		23,300		$2T_{1g}$, $2A_{1g}$ <--- $2T_{2g}$
		16,168		$2T_{2g}$, $2E_g$ <--- $2T_{2g}$
[Ru{(C ₆ H ₅) ₃ As} ₂ (Iz) ₃]	(XIII)	30,303		c.t.
		23,584		$2T_{1g}$, $2A_{1g}$ <--- $2T_{2g}$
		16,891		$2T_{2g}$, $2E_g$ <--- $2T_{2g}$
		14,084		$2A_{2g}$, $2T_{1g}$ <--- $2T_{2g}$
		12,987		$4T_{2g}$ <--- $2T_{2g}$
[Ru{(C ₆ H ₅) ₃ As} ₂ (MeIz) ₃]	(XIV)	30,000		c.t.
		23,616		$2T_{1g}$, $2A_{1g}$ <--- $2T_{2g}$
		17,000		$2T_{2g}$, $2E_g$ <--- $2T_{2g}$
		14,122		$2A_{2g}$, T_{1g} <--- $2T_{2g}$
		12,817		$4T_{2g}$ <--- $2T_{2g}$
[Ru{(C ₆ H ₅) ₃ P} ₂ (Iz) ₂]	(XV)	16,129+		c.t.
[Ru{(C ₆ H ₅) ₃ P} ₂ (MeIz) ₂]	(XVI)	16,223+		c.t.

* Non SI unit employed B.M. = $0.9274 \times 10^{-23} \text{ JT}^{-1}$.

+ Recorded in solid state.

CHAPTER-IV

STUDY OF REACTIONS OF N-TRIMETHYLSILYLMIDAZOLE
AND N-TRIMETHYLSILYL-2-METHYLMIDAZOLE TOWARDS
ANHYDROUS METAL CHLORIDES AND THEIR
DERIVATIVES; SYNTHESIS AND PHYSICO-CHEMICAL
STUDIES ON Ni(II), Pd(II) AND Pt(II)
IMIDAZOLATES AND MIXED LIGAND IMIDAZOLATES

INTRODUCTION

Reactivity of $(\text{CH}_3)_3\text{Si}-$ group in the reagents N-trimethylsilylimidazole/-2-methylimidazole towards C-Cl bond and for M-Cl bond too, is apparently due to the affinity of the $(\text{CH}_3)_3\text{Si}-$ group in these reagents for chlorine to form $(\text{CH}_3)_3\text{SiCl}$. It has been shown that this affinity is also exhibited¹⁸⁶ in reagents like $[(\text{CH}_3)_3\text{Si}]_2\text{X}$ (X=S, Se or Te) which produced novel transition metal chalcogen clusters when reacted with derivatives like $[\text{M}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (M=Co or Ni). This chapter deals an extension of the investigation on the study of the reactivity of the title reagents towards NiCl_2 , PdCl_2 , $[\text{PdCl}_2.(\text{CH}_3\text{CN})_2]$, $[(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni.I}]$, $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$, $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ and $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ and the new compounds isolated have been characterized using the physico-chemical methods as have been described in chapter-II.

EXPERIMENTAL

Reagents Used:

Palladium chloride, platinum chloride, triphenylphosphine (all S.R.L.), nickel chloride, acetic anhydride (both B.D.H., England), glacial acetic acid (Glaxo-India), acetonitrile (Riedel, Germany) all were commercial pure samples and used as received. $[(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni.I}]$ was a gift sample. The reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole were prepared as described in chapter-III. Solvents, ether, n-heptane, chloroform, dichloromethane, petroleum-ether (pet.-ether), n-hexane, tetrahydrofuran (THF), benzene were dried before use.

PREPARATION OF PRECURSORS:

Dehydration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ¹⁵⁸: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10.0 gm) was mixed with 60 ml acetic anhydride and heated in an inert atmosphere for 1 hr., filtered and dried in vacuo giving yellow coloured crystalline solid.

Preparation of dichlorobis(triphenylphosphine)nickel(II)¹⁸⁷: A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.19 gm, 5.0 mmol) dissolved in minimum volume of water was diluted with 25 ml. glacial acetic acid, triphenylphosphine (2.62 gm, 10.0 mmol) taken in 50 ml glacial acetic acid was added to the above solution. The olive green microcrystalline solid separated out of the mother liquor was left standing for 24 hrs., yielded dark

green crystals. It was filtered off, washed with glacial acetic acid and dried in vacuum desiccator. [M.pt 244°C].

Preparation of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ ¹⁸⁸: PdCl_2 (0.355 gm, 2.0 mmol) was stirred with acetonitrile. The colour of the solution changed to yellowish brown by the dissolution of PdCl_2 . It was then refluxed for 1 hr. The yellow solid was obtained when this yellowish brown solution was mixed with pet.-ether.

Synthesis of $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ ¹⁵⁹: Melted triphenylphosphine (1.69 gm, 6.0 mmol) was treated with palladium chloride (0.40 gm, 2.25 mmol). The yellow product that was formed and the excess ligand were extracted with CHCl_3 . The extract was then mixed with n-heptane, yellow solid precipitated out of the solution. The solid was filtered off, washed with n-heptane and dried in vacuo. [M.pt. 298-300°C with decomposition].

Preparation of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ ¹⁵⁹: Melted triphenylphosphine (1.6 gm, 6.0 mmol) was treated with platinum chloride (0.532 gm, 2.0 mmol). The light yellow product that was formed and the excess ligand were extracted in CH_2Cl_2 . This solution was centrifuged to remove suspended particles. The solution was mixed with n-heptane producing colourless compound which was filtered off, washed with n-heptane. White crystalline solid was dried in vacuo [M.pt. 300-310°C].

PREPARATION OF THE COMPLEXES:

Reaction of N-trimethylsilylimidazole with anhydrous NiCl_2 ; Preparation of the bis(imidazolato)nickel(II), (XVII): N-trimethylsilylimidazole (0.70 gm, 5.0 mmol) diluted in 50 ml THF was added dropwise to NiCl_2 (0.32 gm, 2.50 mmol) suspended in 150 ml THF with continuous stirring at room temperature under dry nitrogen atmosphere. When all of the reagent had been dropped, the reaction mixture was vigorously stirred for additional 1 hr. It was filtered off to remove the unreacted NiCl_2 impurity and then vacuum dried, washed several times with pet.-ether to obtain amorphous solid. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt. 190°C].

Reaction of N-trimethylsilyl-2-methylimidazole with anhydrous NiCl_2 , Preparation of bis(2-methylimidazolato)nickel(II), (XVIII): NiCl_2 (0.32 gm, 2.50 mmol) was suspended in 140 ml THF with continuous stirring, to which the reagent N-trimethylsilyl-2-methylimidazole (0.77 gm, 5.0 mmol) diluted in 50 ml THF was added dropwise at room temperature. A light green coloured solid immediately appeared in the solution. The reaction mixture was further stirred for Ca. 2 hrs. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt. 200°C].

Reaction of $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilylimidazole affording bis(imidazolato) nickel(II), (XVII): The reagent N-trimethylsilylimidazole (0.56 gm, 4.0 mmol)

diluted in 40 ml THF was dropped to a solution of $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.30 gm, 2.0 mmol) in 100 ml THF in an atmosphere of dry nitrogen with continuous stirring. An immediate change in colour of the solution was observed from dark green to light pea green. It was vacuum dried giving a green oily mass which after several washings with pet.-ether resulted in pea green microcrystalline solid. The crude was recrystallized in $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ [M.pt. 190°C]. The pet.-ether washings on evaporation gave colourless microcrystalline solid (Ca 1.0 gm i.e. 2.0 mole equivalent of the precursor) which has been identified as $(\text{C}_6\text{H}_5)_3\text{P}$ from M.Pt., i.r. and analytical data.

Reaction of $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole affording bis(2-methylimidazolato)nickel(II), (XVIII): Bis(2-methylimidazolato)nickel(II) was obtained following the same procedure as described above for (XVII) by taking the reagent N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) in 40 ml THF and the precursor $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.308 gm, 2.0 mmol) dissolved in 100 ml THF. The green coloured crude mass was washed with pet.-ether and recrystallized in $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ mixture [M.pt. 200°C]. Here too the washings have afforded free $(\text{C}_6\text{H}_5)_3\text{P}$ in quantitative yield i.e. about 2.0 mole equivalent of the precursor.

Reaction of (η^5 -cyclopentadienyl) (triphenylphosphine)nickel (II)iodide with N-trimethylsilylimidazole; Isolation of bis(η^5 -cyclopentadienyl)bis (μ -imidazolato)bis(triphenylphosphine)dinickel(II), (XIX): To a solution of [$(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni.I}$] (0.35 gm, 0.70 mmol) in THF (15 ml), the reagent N-trimethylsilylimidazole (0.09 gm, 0.70 mmol) was added with stirring. The colour of the solution darkened and within few minutes microcrystalline dark coloured solid started appearing in the solution. Mother liquor was concentrated under vacuo, mixed with hexane and kept at 5°C for a few days. Dark violet microcrystalline solid formed which was filtered off and dried in vacuo [M.pt. > 360°C].

Reaction of (η^5 -cyclopentadienyl) (triphenylphosphine) nickel(II)iodide with N-trimethylsilyl-2-methylimidazole; Isolation of bis(η^5 -cyclopentadienyl)bis(μ -2-methylimidazolato)bis(triphenylphosphine)dinickel(II), (XX): It was synthesized in the same manner as described above for the reaction of its imidazolate analogue. The reagent N-trimethylsilyl-2-methylimidazole (0.11 gm, 0.70 mmol) was added to a continuously stirred solution of the [$(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni.I}$] (0.35 gm, 0.7 mmol) in THF. The dark coloured solid was isolated as above [M.pt. > 360°C].

Reaction of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with N-trimethylsilylimidazole; Formation of dichlorobis (μ -imidazolato)bis(methylcyanide) dipalladium (II), (XXI): The suspension of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.51 gm, 2.0 mmol) in excess CH_3CN was reacted with N-trimethylsilylimidazole (0.56 gm, 4.0 mmol). The colour of the solution that was initially yellowish-brown gradually changed to yellow. The reaction mixture was concentrated to one third of its original volume. Yellow coloured solid started appearing out of the solution which was isolated under inert atmosphere of dry nitrogen as described earlier [M.pt. 230°C with decomposition].

Reaction of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with N-trimethylsilyl-2-methylimidazole; Preparation of dichlorobis (μ -2-methylimidazolato)bis(methylcyanide)dipalladium(II), (XXII): The reagent N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) diluted in 20 ml benzene was added dropwise to a continuously stirred suspension of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.51 gm, 2.0 mmol) taken in CH_3CN . The yellow coloured solid compound obtained as above was filtered, washed with benzene and vacuum dried [M.pt. 245°C].

Reaction of $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilylimidazole; Isolation of dichlorobis (μ -imidazolato)bis(triphenylphosphine)dipalladium(II), (XXIII): $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (0.10 gm, 0.14 mmol) was dissolved in 40 ml benzene and to this solution the reagent N-trimethylsilylimidazole (0.04 gm,

0.28 mmol) has been added with continuous stirring. The colour of the solution immediately got intensified and microcrystalline solid started appearing out of the reaction mixture. The solution was dried in vacuo, light yellow solid that was isolated was washed with CH_2Cl_2 to wash away the impurity of the unreacted starting materials and dried in vacuo. [M.pt. $225-230^\circ\text{C}$]. Washings were dried in vacuo giving 0.037 gm of colourless crystalline solid [M.pt. 80°C] being identified as free $(\text{C}_6\text{H}_5)_3\text{P}$ (1.0 mole equivalent with respect to the precursor).

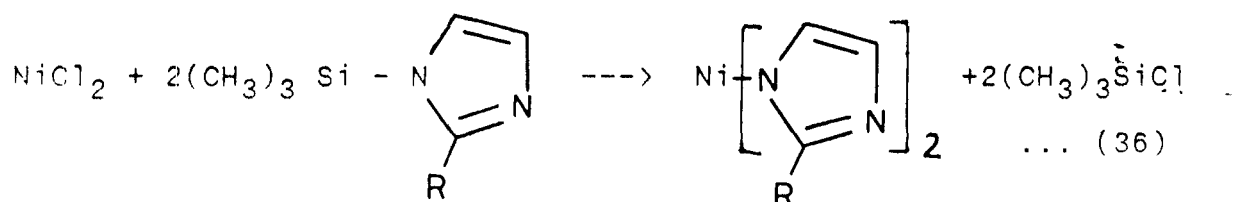
Reaction of $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole, Preparation of dichlorobis-2-methylimidazolato)bis(triphenylphosphine)dipalladium(II), (XXIV): It was prepared in the same manner as described above for (XXIII) by reacting $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (0.10 gm, 0.14 mmol) in 40 ml benzene with the reagent N-trimethylsilyl-2-methylimidazole (0.05 gm, 0.30 mmol). In this case too, the product obtained was washed with CH_2Cl_2 and CHCl_3 to wash away the unreacted starting materials. The light yellow coloured solid was washed repeatedly with ether and both the washings ($\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ and ether) were dried to give white shining crystals that was identified as free $(\text{C}_6\text{H}_5)_3\text{P}$ from its M.pt., i.r. and analytical data, which was equivalent to one mole of the precursor. The main product was dried in vacuo [M.pt. 235°C].

Reaction of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with the reagent N-trimethylsilylimidazole; Isolation of bis(imidazolato) bis(triphenylphosphine) platinum(II), (XXV): $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (0.28 gm, 0.35 mmol) was dissolved in 20 ml CH_2Cl_2 and the reagent N-trimethylsilylimidazole (0.10 gm, 0.70 mmol) was added dropwise. Immediately white turbidity appeared in the solution. It was further stirred for 2 hrs. Hexane (20 ml) was mixed to the reaction mixture to enhance crystallization and kept at 5°C temperature for 24 hrs. white shining crystalline solid appeared in the solution. The solid was washed first with ether and then with CH_2Cl_2 and dried in vacuo [M.pt. 120°C].

Reaction of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato) bis(triphenylphosphine) platinum(II), (XXVI): The reagent N-trimethylsilyl-2-methylimidazole (0.12 gm, 0.80 mmol) was added to a continuously stirred solution of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (0.31 gm, 0.4 mmol) dissolved in 40 ml CH_2Cl_2 . The white coloured solid obtained as above was washed with ether and dried in vacuo [m.pt. 128°C].

RESULTS AND DISCUSSION

Reaction of N-trimethylsilylimidazole/N-trimethylsilyl-2-methylimidazole with anhydrous NiCl_2 and $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$; Isolation of bis(imidazolato) nickel(II), (XVII) and bis(2-methylimidazolato) nickel(II), (XVIII): Reactions of anhydrous NiCl_2 with N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole have produced the product identified as $[\text{NiL}_2]$ (L=imidazolate or 2-methylimidazolate) from its molecular weight and analytical data (Table-IX) in conformity with the replacement of both the chlorines by imidazolate moieties as shown below.



R = H (XVII)

R = CH_3 (XVIII) .

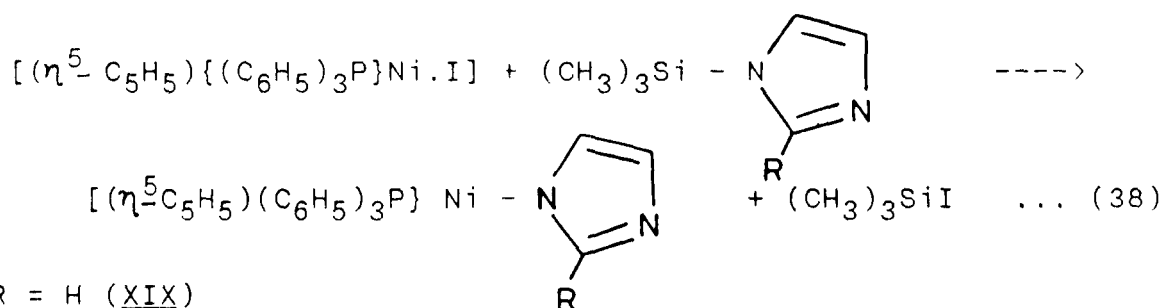
Reaction of the reagent(s) with the precursor $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ has proceeded with the liberation of coordinated $(\text{C}_6\text{H}_5)_3\text{P}$ as free in the solution (Experimental Section) with the formation of quantitative amount of the product identical in nature to that of (XVII) or (XVIII). The analytical data have confirmed the stoichiometries of the

imidazole ring vibrations which are slightly shifted from their positions observed in free imidazole^{42,89-94}. The absence of strong bands particularly at Ca. 500 cm^{-1} in addition to other characteristic of $(\text{C}_6\text{H}_5)_3\text{P}$ in the complexes corroborates the mode of reaction as shown by equation (36). A band at about 390 cm^{-1} is due to ν (M-N) stretching vibration, the position is at considerably higher energy compared to that reported⁴² in $[\text{Ni}(\text{IzH})_6(\text{ClO}_4)_2]$ at 262 cm^{-1} which may be ascribed to the π -donor nature of the ligand similar to that reported^{153, 164, 167} for $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (M=Co, Zn, Cd or Hg) and $[\text{CoLCl}]$ (L=imidazolate or 2-methylimidazolate).

The results of the electronic spectra and magnetic susceptibility measurements are summarized in Table-XI. The nature of electronic spectra recorded in non-polar solvents is identical to the reflectance spectra of the solids indicating the existence of the similar species in solution as well as in solids. The recorded band positions in the complexes (XVII) and (XVIII) are characteristic of a diamagnetic square-planar Ni(II) complex¹⁷⁵. However, the observed abnormal magnitude of μ_{eff} (Ca. 1.0 B.M.) favours some paramagnetism in the complex. The ground electronic state of Ni(II) complexes (singlet diamagnetic or triplet paramagnetic) is exceptionally sensitive to geometry and/or

the strength of the ligand field¹⁸⁹. The square-planar nickel(II) complexes are generally considered to be diamagnetic (singlet ground state $^1A_{1g}$). However, the ligand field treatment by Ballhausen and Liehr¹⁴⁴ suggests that square planar configuration may be retained even in triplet ground state. It is quite possible that $[NiL_2]$ is basically square-planar with $^1A_{1g}$ ground state but mixed with or in equilibrium with some paramagnetic species with $^3A_{1g}$ ground state. Precedence for such behaviour is known^{190,191}. A spin state isomerism¹⁹² may also be visualized. In other words the energy levels of different multiplicities are positioned with kT of each other making the complexes near the magnetic cross over point whereby population of both states become equally probable.

Reaction of $[(\eta^5-C_5H_5)\{(C_6H_5)_3P\}Ni.I]$ with the reagent N-trimethylsilylimidazole/2-methylimidazole; Isolation of bis(cyclopentadienyl)bis(μ -imidazolato)bis(triphenyl phosphine)dinickel(II), (XIX) and bis(cyclopentadienyl)bis(μ -2-methylimidazolato)bis(triphenylphosphine)dinickel(II), (XX): The analytical data (Table-VI) of the products obtained from the reaction of $[(\eta^5-C_5H_5)\{(C_6H_5)_3P\}Ni.I]$ with the reagent N-trimethylsilylimidazole/2-methylimidazole are compatible with the stoichiometry as $[(\eta^5-C_5H_5)\{(C_6H_5)_3P\}-Ni.L]_2$ suggesting the reaction as following:



R = H (XIX)

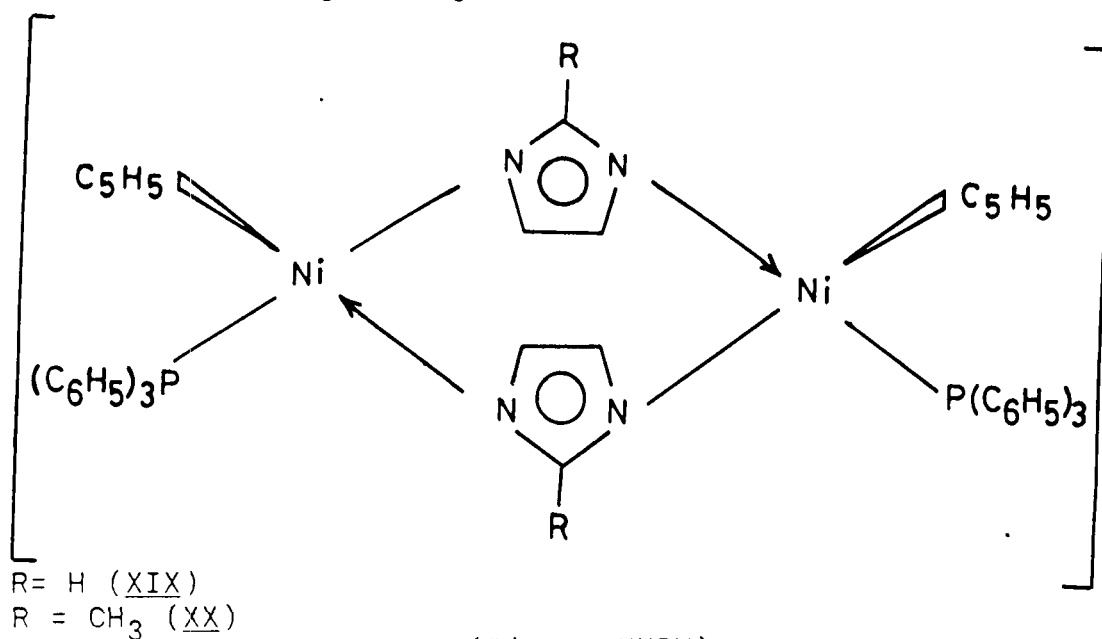
R = CH₃ (XX)

The molar conductance values and the experimentally determined molecular weight (Table-IX) of the compounds (XIX) and (XX) are indicative of non-electrolytic and dimeric nature of the complexes. It is evident from the i.r. and ¹H n.m.r. spectral studies (Table-X) of the compounds that the molecule retains the cyclopentadienyl ring as well as the triphenylphosphine as coordinated to metal ion. Characteristic imidazole ring vibrations in i.r. spectra are slightly shifted from their positions in the free ligand^{42,89-94}. The ν (M-N) stretching frequency appears at 400 cm⁻¹.

The ¹H n.m.r. spectrum (Table-X) of the compounds contained a singlet at 4.0δ with a number of multiplets spanning in 7.8-7.0δ assignable to the protons of C₅H₅ ring and that of coordinated (C₆H₅)₃P and imidazolate moiety respectively.

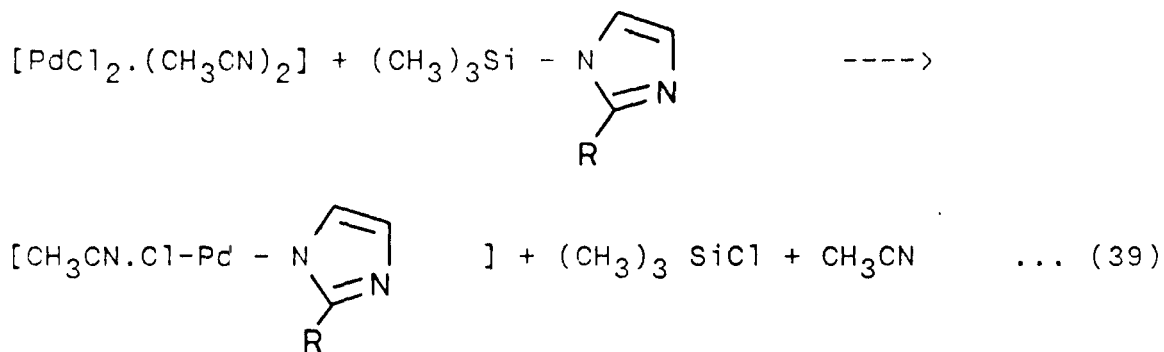
The observed μ_{eff} value of 3.4 B.M. for the complexes (Table-XI) is consistent with 2 unpaired spin of the d⁸ configuration of the ion¹⁷⁴.

The reflectance spectrum exhibits a single band at $17,000\text{ cm}^{-1}$ (Table-XI) indicative of a tetrahedral environment ¹⁷⁵ around nickel(II). The electronic spectrum recorded in a coordinating solvent, DMSO, the only solvent in which the complex is completely soluble (giving violet colouration) exhibited strong bands at $34,000\text{ cm}^{-1}$, $17,000\text{ cm}^{-1}$ with a shoulder at $30,000\text{ cm}^{-1}$ and a weak broad band at $11,000\text{ cm}^{-1}$. The extinction coefficient ϵ of the bands are generally very high ($\epsilon \approx 10^3$) suggesting that tetrahedral species are still present in the solution in combination with the octahedral species resulted in due to coordination by DMSO solvent ¹⁷⁵. Since the complex has a partial solubility in the non-coordinating solvent while completely dissolves in coordinating solvents like DMSO, CH_3CN etc... hence forth favouring a dimeric structure reasonably through imidazolate bridges as given below.



(Figure-XXIV)

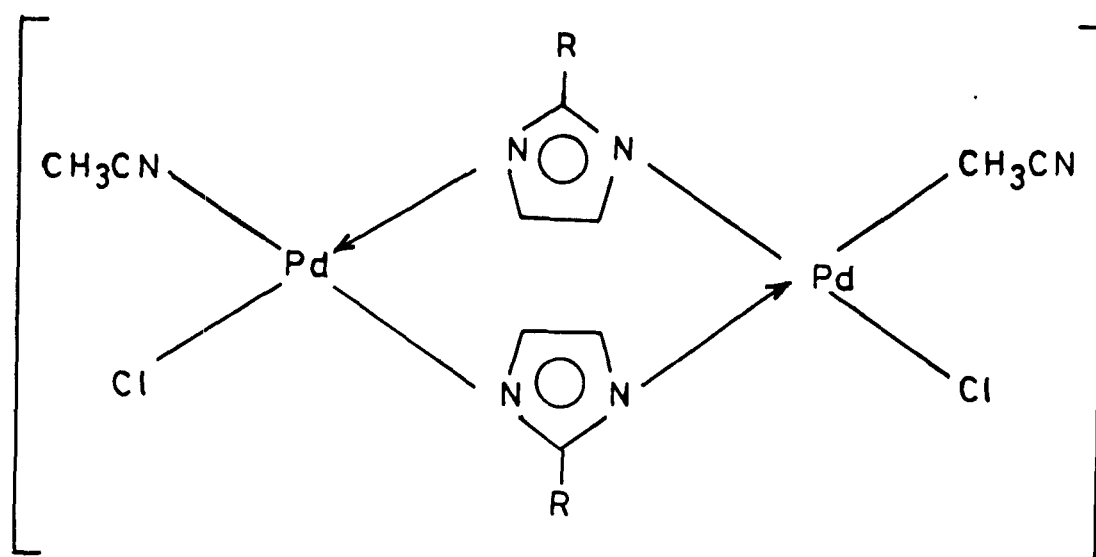
Reaction of N-trimethylsilylimidazole/2-methylimidazole with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ and $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$; Isolation of dichlorobis(μ -imidazolato)bis(methylcyanide)dipalladium(II), (XXI); dichlorobis (μ -2-methylimidazolato)bis(methylcyanide)dipalladium(II), (XXII): dichlorobis(μ -imidazolato)bis(triphenylphosphine)dipalladium(II), (XXIII) and dichlorobis(μ -2-methylimidazolato)bis(triphenylphosphine)dipalladium(II), (XXIV): The substrate $[\text{PdCl}_2.(\text{CH}_3\text{CN})_2]$ obtained in-situ by refluxing palladium chloride in CH_3CN was reacted with the reagents. N-trimethylsilyl-imidazole/2-methylimidazole. Analytical data of the products of the reactions are in conformity with the stoichiometry as $[\text{PdLC1.CH}_3\text{CN}]_x$ compatible with the reaction as following:



R = H (XXI)
R = CH_3 (XXII)

The compounds are non-electrolyte in nature and exist in dimeric form as evidenced from the conductivity and molecular weight measurements (Table-IX). The presence of CH_3CN as well as of chlorine in the coordination sphere has been further verified from the i.r. spectroscopic investigation of the

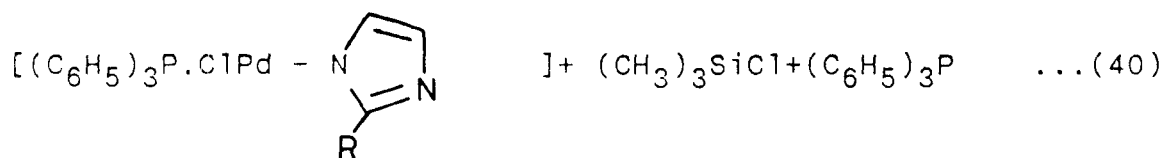
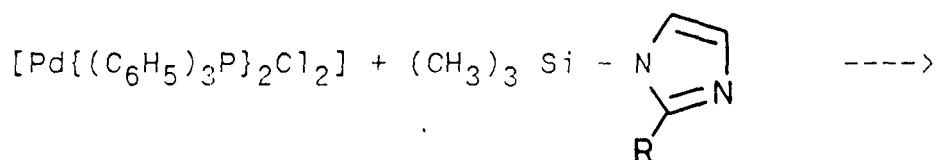
compounds (vide infra). The electron count following the procedure described earlier suggest that the Pd(II) in $[\text{PdLCI} \cdot \text{CH}_3\text{CN}]_x$ attains $16e^-$ in its shell. The central metal ion is apparently electronically as well as coordinatively unsatisfied, which become satisfied through bridging via one of the ligands similar to that known¹⁹³⁻¹⁹⁷ for a number of dimeric palladium complexes involving ligand and/or chlorine bridges. The physico-chemical data presented here favour imidazolate bridging in the complexes (XXI) and (XXII). The i.r. spectrum (Table-X) exhibits a broad weak band in $2100-2200 \text{ cm}^{-1}$ region due to presence of coordinated CH_3CN in the molecule¹²⁶. The characteristic ring vibrations are observed at the appropriate positions^{42,89-94}. The far-i.r. region of the spectrum shows a doublet at $400, 430 \text{ cm}^{-1}$ and a band of medium intensity at 360 cm^{-1} characteristic of ν (Pd-N) and terminal ν (Pd-Cl) stretching vibrations^{198,199} respectively. The observed doublet for ν (Pd-N) may be arising due to the resonance splitting with the probable involvement of both the pyrrolic as well as pyridyl nitrogen in bonding or existence of cis-isomer¹⁹⁸ in the compounds or both. The appearance of band characteristic of terminal ν (Pd-Cl) vibration rules out the possibility of chlorine bridging in the complex. The dimeric formulation $[\text{PdLCI} \cdot \text{CH}_3\text{CN}]_2$ involving imidazolate bridging between the metal ions seems plausible with the molecular representation as shown below in figure-XXV.



R = H (XXI)
 R = CH₃ (XXII)

(Figure-XXV)

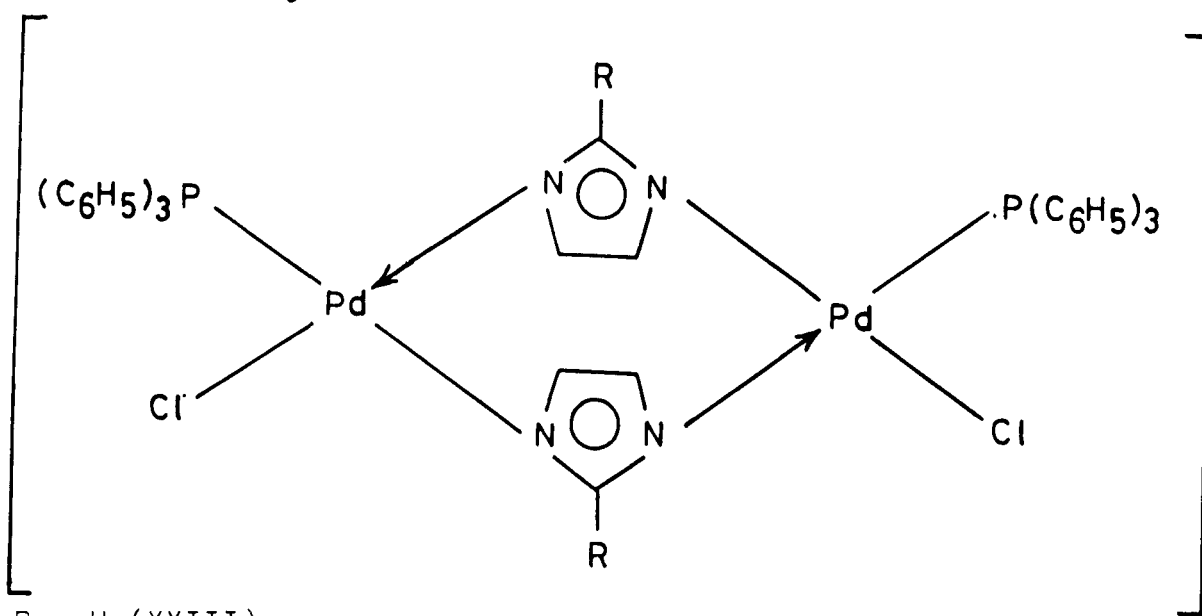
The analytical data (Table-IX) of the products obtained from the reaction of the reagents with $[\text{Pd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ are compatible with the stoichiometry as $[\text{PdClL}(\text{C}_6\text{H}_5)_3\text{P}]_x$ suggesting the mode of reaction as below:



R = H (XXIII)
 R = CH₃ (XXIV)

The compounds are non-electrolyte in nature and exist in dimeric form (Table-IX). Here too, the central metal ion can be visualized to be coordinatively and electronically

dissatisfied forcing dimerization through, preferably, imidazolate bridging as mentioned above for the complexes (XXI) and (XXII). Infra-red spectral studies rule out the possibility of chlorine bridging in the complexes because of the appearance of a band of medium intensity at about 360 cm^{-1} characteristic of terminal ν (Pd-Cl) stretching frequency¹⁹⁹. The characteristic imidazolate^{42,89-94} and triphenylphosphine ring vibrations^{127,185} have been observed at their respective positions though some of them superimposed with each other. The position of the metal-ligand, ν (M-N), bond stretching frequency observed in the complex has been shown in table-X. The molecular presentation involving imidazolate bridging to yield dimer $[\text{PdLCl}(\text{C}_6\text{H}_5)_3\text{P}]_2$ is shown in figure XXVI:



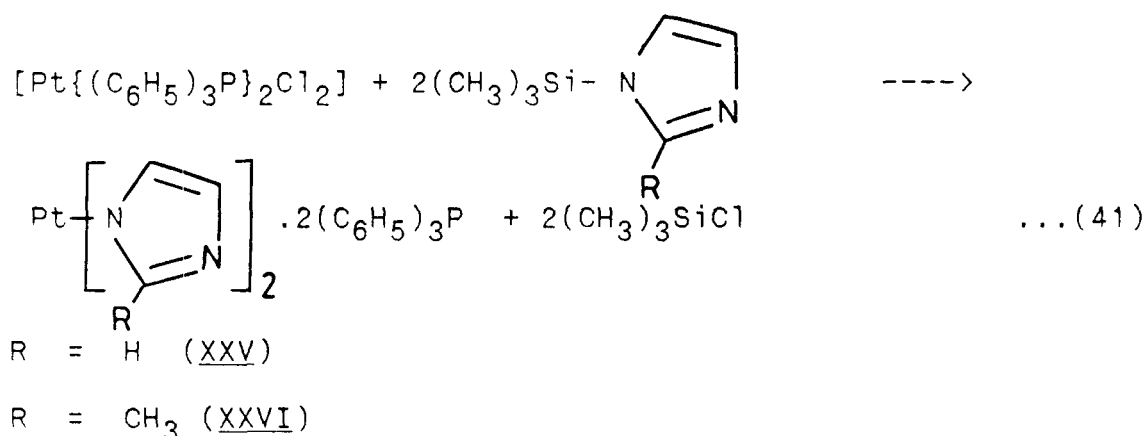
R = H (XXIII)

R = CH₃ (XXIV)

(Figure-XXVI)

The complexes are diamagnetic in nature as expected for d^8 configuration of metal ion in square-planar environment of ligands. The electronic spectrum obtained in DMSO shows three well resolved bands of nearly equal intensity (Table-XI) which can be explained in terms of square-planar geometry of the molecule assignable to those arising from three spin allowed d-d singlet-singlet transitions¹⁷⁵. The transitions, in order of increasing energy are from low lying d-orbitals d_{xy} (b_{2g}); dz^2 (a_{1g}) and d_{xz} , d_{yz} (e_g) to empty $dx^2 - y^2$ (b_{1g}) orbitals designated as ${}^1A_{2g} \leftarrow {}^1A_{1g}$, ${}^1B_{1g} \leftarrow {}^1A_{1g}$ and ${}^1E_g \leftarrow {}^1A_{1g}$ respectively. The bands corresponding to singlet-triplet transition usually expected²⁰⁰ at higher wavelengths i.e. 500-600 nm have not been observed in the present complexes, probably, they are very weak owing to the forbidden nature of the transition. It has been pointed out^{200,201} that the two high energy singlet-singlet transitions i.e. $dz^2 \rightarrow dx^2 - y^2$ (${}^1B_{1g} \leftarrow {}^1A_{1g}$) and $d_{xz}, d_{yz} \rightarrow dx^2 - y^2$ (${}^1E_g \leftarrow {}^1A_{1g}$) are dependent on the nature of the environment usually undergoing shifts while $d_{xy} \rightarrow dx^2 - y^2$ (${}^1A_{2g} \leftarrow {}^1A_{1g}$) transition is least affected to an extent that the position remains unchanged. It can be seen from the (Table-XI) that the position of the band of the lowest energy transition is almost identical in all of the complexes i.e. (XXI), (XXII) and (XXIII), (XXIV).

Reaction of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with the reagents N-trimethylsilylimidazole/2-methylimidazole; Isolation of bis(imidazolato)bis(triphenylphosphine)platinum(II), (XXV) and bis(2-methylimidazolato)bis(triphenylphosphine)platinum (II), (XXVI): The product of the reaction of $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with the reagents has been identified as $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{L}_2]$ where L=imidazolate or 2-methylimidazolate in view of its analytical data and molecular weight measurement (Table-IX) which agree well with its proposed stoichiometry. The reaction for its formation may be represented as below:



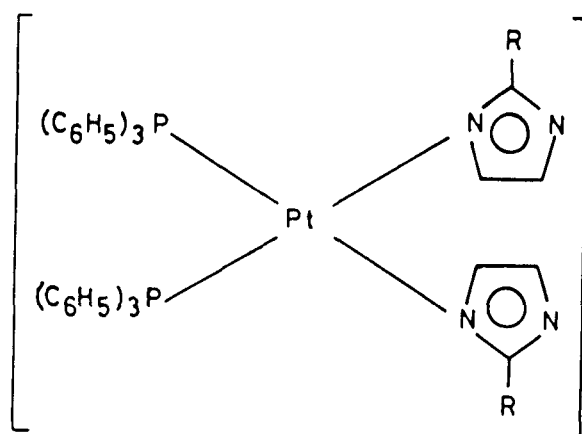
Both the chlorines of the precursor have been substituted by the imidazolate/2-methyl imidazolate moiety. These compounds melt sharply which indicates that they are monomeric in nature, which has further been confirmed by carrying out its molecular weight measurements.

The i.r. spectrum (Table-X) of the compounds (XXV) and (XXVI) shows imidazolate ring vibrations at their appropriate positions^{42,89-94}. It shows all the three modes of the

vibration (q,r,t) of $(C_6H_5)_3P$ at their expected positions¹⁸⁵ though they are slightly shifted from the position in free $(C_6H_5)_3P$ due to coordination to the metal ion. A band of weak intensity at 500 cm^{-1} has been assigned to the metal-nitrogen stretching frequency $\nu(M-N)$ ¹⁹⁸.

The complexes are diamagnetic in nature and the reflectance spectra (Table-XI) of the complexes (XXV) and (XXVI) show three bands at about $21,000\text{ cm}^{-1}$, $25,190\text{ cm}^{-1}$ and $27,000\text{ cm}^{-1}$ arising from the spin allowed d-d transitions from the three low lying d levels to the empty dx^2-y^2 orbital, $^1A_{2g} \leftarrow ^1A_{1g}$, $^1B_{1g} \leftarrow ^1A_{1g}$ and $^1E_g \leftarrow ^1A_{1g}$ respectively in the square-planar geometry of the complex¹⁷⁵. The intense band observed at $35,015\text{ cm}^{-1}$ may be due to metal-ligand charge-transfer excitation.

On the basis of the above observations a square-planar arrangement of ligand around metal ion is proposed as shown below:



R = H (XXV)
R = CH_3 (XXVI)

(Figure-XXVII)

It can be seen from the results of the present investigations that the reactions of N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole with the transition metal precursors $[M\{(C_6H_5)_3P\}_2 Cl_2]$ where M is Ni, Pd, Pt, proceeds with the liberation of two, one or none mole equivalent of free triphenylphosphine in the reaction mixture. It may be due to the inherent nature of the individual precursor i.e. it may be recalled that ligands specially with π -bonding nature like $(C_6H_5)_3P$ etc. in square-planar Pt (II) complexes exhibit labelization for the incoming nucleophile in displacement/substitution reactions. This behaviour is least exhibited in Pd(II) rather of dismal existence (occurrence) in Ni (II) complexes. It is tempting to suggest the present state of affair is probably due to π -acceptor action of triphenylphosphine which is apparently more pronounced due to its labelizing effect in Pt (II) complexes.

TABLE-IX
Analytical data and molar conductance Λ_M ($\text{ohm}^{-1} \text{cm}^2 \text{Mol}^{-1}$) of the complexes.

Complexes		% C		% H		% N		% M		Mol. Wt.		Λ_M $\text{ohm}^{-1} \text{cm}^2$ Mol^{-1}
		Found	(Calcd.)	Found	(Calcd.)	Found	(Calcd.)	Found	(Calcd.)	Found	(Calcd.)	
[Ni(Iz) ₂]	(XVII)	37.0 (37.4)		3.0 (3.1)		28.8 (29.1)		29.5 (30.5)		182 (193)		-
[Ni(MeIz) ₂]	(XVIII)	43.1 (43.5)		4.3 (4.5)		24.9 (25.4)		25.2 (26.6)		208 (221)		-
[$(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni(Iz)}_2$]	(XIX)	68.6 (68.9)		4.9 (5.1)		6.1 (6.2)		12.4 (13.0)		897 (906)		-
[$(\eta^5\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{Ni(MeIz)}_2$]	(XX)	69.1 (69.4)		5.3 (5.4)		5.7 (6.00)		12.1 (12.6)		927 (934)		-
[Pd(Iz)Cl·CH ₃ CN] ₂	(XXI)	23.4 (24.0)		2.4 (2.4)		16.8 (16.8)		42.1 (42.5)		493 (500)		12
[Pd(MeIz)Cl·CH ₃ CN] ₂	(XXII)	27.1 (27.3)		3.0 (3.0)		15.8 (15.9)		39.9 (40.2)		521 (527)		14
[Pd(Iz)Cl·(C ₆ H ₅) ₃ P] ₂	(XXIII)	52.8 (53.5)		3.7 (3.8)		5.9 (5.9)		21.2 (22.5)		934 (941)		17
[Pd(MeIz)Cl·(C ₆ H ₅) ₃ P] ₂	(XXIV)	54.2 (54.5)		4.06 (4.1)		5.8 (5.8)		20.9 (21.8)		962 (969)		20
[Pt(Iz) ₂ ·2(C ₆ H ₅) ₃ P]	(XXV)	58.8 (59.1)		4.3 (4.3)		6.4 (6.6)		21.9 (22.8)		848 (853)		-
[Pt(MeIz) ₂ ·2(C ₆ H ₅) ₃ P]	(XXVI)	59.4 (59.9)		4.4 (4.5)		6.2 (6.4)		21.9 (22.1)		873 (881)		-

TABLE-I

Imidazolate and $(C_6H_5)_3P$ ring, M-N, M-P and M-Cl frequencies (cm^{-1}) observed in the i.r. spectra and 1H .n.m.r. spectra of complexes									
Complexes	Imidazolate ring vibrations				$(C_6H_5)_3P$ - ring vibra- tions	$\nu(C\equiv N)/$ $\eta^5-C_5H_5$	1H .n.m.r.		
	R ₁	R ₂	R ₃	R ₄			$\nu(M-N)$	$\nu(M-P)$	$\nu(M-Cl)$
[Ni(Iz) ₂] (XVII)	1550s	1480m	1420s	1320m	-	-	390s	-	-
[Ni(MeIz) ₂] (XVIII)	1570s	1470m	1420m	1320m	-	-	390s	-	-
$[(\eta^5-C_5H_5)(C_6H_5)_3P]Ni(Iz)_2$ (XIX)	1580s	1480s	1430s	1330m	1480s, 1430s, 1090s, 730s, 800s 510s, 500s	3075s, 1000s, 400s	330m	-	4.0 7-7.6
$[(\eta^5-C_5H_5)(C_6H_5)_3P]Ni(MeIz)_2$ (XX)	1570s	1480s	1420s	1325s	1480s, 1440s, 1110s, 720, 700s, 810s 505m, 500s	3075s, 1000s, 400s	325m	-	2.45 4.0 7-7.6
[Pd(Iz)Cl·CH ₃ CN] ₂ (XXI)	1540s	1480m	1430m	1330m	-	2100 -2150w br. 430m	400s	-	360m - -
[Pd(MeIz)Cl·CH ₃ CN] ₂ (XXII)	1550s	1480m	1420m	1320m	-	2110 -2190m br. 430m	400s	-	360m - -
[Pd(Iz)Cl·CH ₃ (H ₅) ₃ P] ₂ (XXIII)	1550m	1470s	1440s	1330m	14070s, 1440s, 1100s, 750s, 695s, 510s, 500s	- 400s 430m	310w	-	360m - -
[Pd(MeIz)Cl·CH ₃ (H ₅) ₃ P] ₂ (XXIV)	1550m	1480s	1440s	1320m	1480s, 1440s, 1090s, 750s, 700s, 505s, 500m	- 400s 430m	310w	-	360m - -
[Pt(Iz) ₂ ·2(CH ₃ H ₅) ₃ P] (XXV)	1545s	1480s	1440s	1330m	1480s, 1440s, 1100s, 750s, 695s, 560s, 550m	5 500m	310w	-	- - -
[Pt(MeIz) ₂ ·2(CH ₃ H ₅) ₃ P] (XXVI)	1550s	1480s	1435s	1325m	1480s, 1435s, 1090s, 750s, 700s, 550s, 530m	-	500m	310w	- - -

* L = Imidazolate (Iz) or 2-methylimidazolate (MeIz).

TABLE-XI

μ_{eff} (B.M.)^{*} and ligand field bands (cm^{-1}) observed in the reflectance and the electronic spectra of complexes and their assignments.

Complexes	μ_{eff} (B.M.)	Band Position (cm^{-1})	Extinction Coefficient (ϵ)	Assignment
[Ni(Iz) ₂]	(XVII)	0.9	30,300 (29,500)	$1B_{1g} \leftarrow 1A_{1g}$
			23,800 (23,300)	$1A_{2g} \leftarrow$
			14,280 (14,500)	$3A_{2g} \leftarrow$
[Ni(MeIz) ₂]	(XVIII)	1.1	30,350 (30,300)	$1B_{1g} \leftarrow 1A_{1g}$
			23,620 (23,500)	$1A_{2g} \leftarrow$
			14,140 (14,000)	$3A_{2g} \leftarrow$
[($\eta^5\text{-C}_5\text{H}_5$) ₂ (C ₆ H ₅) ₃ P]Ni(Iz) ₂	(XIX)	3.4	17,000	$3T_1(P) \leftarrow 3T_1$
			(34,000)	c.t.
			(30,000)	$3T_{1g}(P) \leftarrow 3A_{2g}$
			(17,000)	$3T_{1g} \leftarrow$
[($\eta^5\text{-C}_5\text{H}_5$) ₂ (C ₆ H ₅) ₃ P]Ni(MeIz) ₂	(XX)	3.5	(11,000)	$3T_{2g} \leftarrow$
			17,000	$3T_1(P) \leftarrow 3T_1$
			(35,714)	c.t.
			(30,300)	$3T_{1g}(P) \leftarrow 3A_{2g}$
			(17,857)	$3T_{1g} \leftarrow$
			(11,111)	$3T_{2g} \leftarrow$
			2,272	
			1,477	
			1,613	
			500	
			2,162	
			1,311	
			1,518	
			512	

Table-XI Contd...

Complexes	μ_{eff} (B.M.)	Band Position (cm^{-1})	Extinction Coefficient (cm^{-1})	Assignment
[Pd(Iz)Cl.CH ₃ CN] ₂	(XXI) Diamag.	(35,714) (32,282) (27,777)	195 194 176	¹ A _{2g} <--- ¹ A _{1g} ¹ B _{1g} <--- ¹ E _g <---
[Pd(MeIz)Cl.CH ₃ CN] ₂	(XXII) -do-	(35,710) (32,218) (27,407)	219 214 202	¹ A _{2g} <--- ¹ A _{1g} ¹ E _g <--- ¹ E _g <---
[Pd(Iz)Cl.(C ₆ H ₅) ₃ P] ₂	(XXIII) -do-	(35,714) (32,203) (26,315)	178 172 169	¹ A _{2g} <--- ¹ A _{1g} ¹ B _{1g} <--- ¹ E _g <---
[Pd(MeIz)Cl.(C ₆ H ₅) ₃ P] ₂	(XXIV) -do-	(35,706) (32,199) (27,619)	304 300 303	¹ A _{2g} <--- ¹ A _{1g} ¹ B _{1g} <--- ¹ E _g <---
[Pt(Iz) ₂ .2(C ₆ H ₅) ₃ P]	(XXV) -do-	35,105 27,000 25,190 21,000	- - - -	c.t. ¹ E _g <--- ¹ A _{1g} ¹ B _{1g} <--- ¹ A _{2g} <---
[Pt(MeIz) ₂ .2(C ₆ H ₅) ₃ P]	(XXVI) -do-	34,733 27,118 25,000 21,413	- - - -	c.t. ¹ E _g <--- ¹ A _{1g} ¹ B _{1g} <--- ¹ A _{2g} <---

Positions in CH₂Cl₂/DMSO solution given in parenthesis. * Non SI unit employed
B.M.=0.9274 × 10⁻²³ JT⁻¹

CHAPTER-V

STUDY OF REACTIONS OF N-TRIMETHYLSILYLIMIDAZOLE AND N-TRIMETHYLSILYL-2-METHYLIMIDAZOLE TOWARDS ANHYDROUS METAL CHLORIDES AND THEIR DERIVATIVES; SYNTHESIS AND CHARACTERIZATION OF BIS(IMIDAZOLATO)DIALKYL TIN(IV) AND COVALENT TIN(II) IMIDAZOLATES AS WELL AS THE MIXED LIGAND IMIDAZOLATES OF Sn(IV), Sn(II), Zn(II), Cd(II) AND Hg(II), IONS

INTRODUCTION

Organotin(IV) compounds containing covalently bonded N-derivatives specially that with linear amido group have been the subject of considerable investigations²⁰² during the last two decades or so. The reactivity of such derivatives towards nucleophilic reagents like CS_2 , $(\text{C}_6\text{H}_5)_3\text{P}$, RNCS etc. has been investigated^{203,204} by previous workers and it has been concluded that in majority of the cases insertion between $\text{Sn}^{\text{IV}}\text{-N}$ bonds takes place under normal conditions. Comparatively, less interest has been shown towards the preparation of organotin (IV) derivatives incorporating π -delocalized N-heterocycles specially imidazole or its 2-methyl derivative, which are now well recognized as $4e^-$ donor (through additional π -donating capability). N-trialkyltin and N-triphenyltin-derivatives of pyrazole, imidazole or triazole have been prepared in the past by utilizing the condensation of the azoles with bis(tri-butyltin)oxide, bis(trimethyltin)oxide or bis(triphenyltin)oxide²⁰⁵ as the only suitable route. Another preparative method utilizing the 1,3 dipolar cycloaddition of tri-n-butyltinazide to diethylacetylene dicarboxylate has also been described²⁰⁶⁻²⁹⁸ in the literature. The condensation reactions as well as the 1,3-cycloaddition process have always, produced²⁰⁹ the trialkyltin(IV) or triphenyltin(IV) derivatives i.e. R_3SnIz as the major product. All of these synthetic procedures, however, could

not prove success for the preparation of the corresponding R_2SnIz_2 derivatives rather R_3SnIz is always obtained as the ultimate product. One of the foremost reasons could be the decomposition of the extremely moisture sensitive R_2SnIz_2 to its hydrolytically stable R_3SnI_2 analogue. Furthermore, the chemistry of covalent tin(II) compounds has been comparatively less explored area of research. There are only a few well characterized covalent tin(II) compounds. This is considered to be due to the imposition of the low coordination number of two, providing six rather than eight valence electrons, making these molecules electron deficient. These molecules are, therefore, susceptible to associate unless prevented by the use of bulky substituent^{204,210}. Some of these compounds have been characterized in the recent past, using X-ray crystal structure determination²¹¹⁻²¹³. With smaller organic substituent like that in bis(dimethylamido)-tin(II), the association into a dimer has, recently, been confirmed²¹⁴. The use of linear amido groups (simpler or bulky) has in general been exploited for the preparation of covalent tin(II) derivatives. However, no attempt has so far been made to explore the use of N-heterocycles. It is evident from the previous chapters that N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole is a potent reagent for the preparation of monomeric moisture sensitive transition metal imidazoles with covalent M-N bonds. This chapter describes the syntheses

and characterization of a few organotin(IV) imidazoles, mixed ligand imidazoles and tin(II) imidazoles. Reactions of the reagents towards $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$, $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ and $[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ have also been examined and described in this chapter.

EXPERIMENTAL

Reagents Used:

All the reagents used were commercially pure samples, dimethyltin dichloride (E.Merck), triphenylphosphine(S.R.L., India) zinc chloride (E. Merck), cadmium chloride(Loba) mercuric chloride (E. Merck), pyridine N-oxide(B.D.H., England) iodine (B.D.H., England) have been used as received excepting $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (B.D.H., England) which was dehydrated²¹⁵ before use. Tribenzyltinchloride was prepared and recrystallized as reported elsewhere²¹⁶. N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole were prepared as has been described in chapter-III. Solvents, tetrahydrofuran, benzene, n-hexane, ether, etc. were dried before use.

PREPARATION OF THE PRECURSORS:

Dehydration of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ²¹⁵: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (5.0gm) was dehydrated by refluxing it in acetic anhydride for 3 hrs. The reaction mixture was filtered, washed 2-3 times with ether and dried in vacuum desiccator.

Preparation of tribenzyltinchloride²¹⁶: Tin powder(15.0 gm) was added in 40 ml 10% NaOH solution in a stoppered flask and vigorously shaken for about 10-15 minutes. The powder was washed by decantation with water until each washing of

water shows no alkalinity to litmus paper then washed it with methanol, dried and crushed to fine powder.

A mixture of 9.0 gm of purified tin powder and 75 ml of water was vigorously shaken in a flask. The reaction mixture was heated to boil then 9 ml benzyl chloride was added dropwise over a period of 3-4 mts. Refluxed it for 2-3 hrs. and the solid obtained was filtered off and air dried. This solid was extracted with hot ethyl acetate and filtered in hot condition. Filtrate was collected and evaporated at room temperature. The crude was recrystallized from hot glacial acetic acid and air dried [M.pt 140°C].

Preparation of dichlorobis(triphenylphosphine)zinc(II), $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ ²¹⁷: Anhydrous zinc chloride (0.68 gm, 5.0 mmol) was dissolved in ether (50 ml) and it was added to the triphenylphosphine (2.62 gm, 10.0 mmol) in dry benzene. Colourless shining crystalline mass started to come out of the solution. The solid was filtered and dried in air [M.pt. 295°C].

Preparation of dichlorobis(triphenylphosphine)cadmium(II), $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ ²¹⁸: Triphenylphosphine (2.62 gm, 10.0 mmol) was dissolved in hot ethanol (100 ml) and cadmium chloride (1.0 gm, 5.0 mmol) dissolved in hot ethanol (50 ml) was added to it. On cooling colourless crystals appeared, filtered and washed with alcohol, dried in air [M.pt. 245°C].

Preparation of dichlorobis(triphenylphosphine)mercury(II), $[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]^{218}$: Mercuric chloride(1.3 gm, 5.0 mmol) was dissolved in hot alcohol(50 ml) and triphenylphosphine(2.6 gm, 10.0 mmol) dissolved in hot alcohol(100 ml) were rapidly mixed. Colourless shining crystals of dichlorobis(triphenylphosphine) mercury(II) were separated and dried in air [M.pt.273°C followed by decomposition].

PREPARATION OF THE COMPLEXES:

Reaction of dimethyltin dichloride with N-trimethylsilylimidazole; Isolation of bis(imidazolato)dimethyltin (IV), (XXVII):: The reagent N-trimethylsilylimidazole(0.56 gm, 4.0 mmol) in hexane(10 ml) was dropped to a solution of dimethyltin-dichloride(0.44 gm, 2.0 mmol) in 40 ml hexane with stirring at room temperature under dry nitrogen atmosphere. The reaction mixture was stirred for an hr. yielding colourless polycrystalline mass which was kept overnight at 5°C to ensure complete separation of the mass from the mother liquor. It was filtered off, washed with n-hexane and dried in vacuo and recrystallized from CH_2Cl_2 /n-hexane [M.pt.68-70°C].

Reaction of dimethyltin dichloride with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato) dimethyltin(IV), (XXVIII):: The reaction was performed in the same way as described above for (XXVII) by taking the reagent

N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) in 15 ml hexane and dropping it to a solution of dimethyltindichloride (0.44 gm, 2.0 mmol) with stirring in 30 ml hexane. White microcrystalline mass thus obtained was washed with hexane, dried in vacuo and recrystallized from CH_2Cl_2 /n-hexane mixture [M.pt.84°C].

Reaction of dibutyltindichloride with N-trimethylsilylimidazole; Formation of bis(imidazolato)dibutyltin(IV), (XXIX): To a solution of dibutyltindichloride (0.61 gm, 2.0 mmol) in 60 ml hexane the reagent N-trimethylsilylimidazole(0.56 gm, 4.0 mmol) was added dropwise with continuous stirring. The reaction mixture was stirred for Ca. 3 hrs. and the resulting solid was filtered off, washed with hexane and dried in vacuo giving a very hygroscopic solid [M.pt.64°C].

Reaction of dibutyltindichloride with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato)dibutyltin(IV), (XXX): The reagent N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) diluted in 15 ml hexane was continuously dropped to dibutyltindichloride(0.61 gm, 2.0 mmol) in 50 ml hexane in the dry nitrogen atmosphere. The reaction mixture was further stirred for Ca.3 hrs. The solid that appeared in the solution was filtered off, washed with n-hexane and dried in vacuo. The crude was recrystallized

from CH_2Cl_2 /n-hexane mixture yielding moisture sensitive white solid [M.pt.72-74°C].

Reaction of tribenzyltinchloride with N-trimethylsilylimidazole; Isolation of (imidazolato) tribenzyltin(IV), (XXXI): Tribenzyltinchloride (0.86 gm, 2.0 mmol) was dissolved in 30 ml CH_2Cl_2 to which the reagent N-trimethylsilylimidazole (0.28 gm, 2.0 mmol) was added with continuous stirring. White solid immediately appeared in the solution. It was stirred for 3 hrs. The reaction mixture was kept at about 5°C temperature overnight then filtered, washed with ether and dried in vacuo [M.pt.60°C].

Reaction of tribenzyltinchloride with N-trimethylsilyl-2-methylimidazole; Isolation of (2-methylimidazolato) tribenzyltin(IV), (XXXII). It was prepared by reacting equimolar amount of tribenzyltinchloride (1.28 gm, 3.0 mmol) with the reagent N-trimethylsilyl-2-methylimidazole (0.46 gm, 3.0 mmol) with continuous stirring. The colourless microcrystalline solid that slowly appeared with stirring was further stirred for 4 hrs. and kept at 5°C for crystallization. Filtered and washed thoroughly with ether and dried in vacuo [M.pt.72°C].

Reaction of anhydrous stannous chloride with N-trimethylsilylimidazole; Isolation of bis(imidazolato)dichloroditin(II), (XXXIII): To a solution of anhydrous stannous chloride (0.38 gm, 2.0 mmol) in 20 ml THF, the reagent

N-trimethylsilylimidazole (0.70 gm, 5.0 mmol) diluted with 10 ml THF was added with continuous stirring at room temperature in dry nitrogen atmosphere. The reaction mixture was then stirred for an additional 3 hrs. and resulting solid was filtered off, washed with THF and dried in vacuo giving a hygroscopic solid. It was recrystallized from CH_2Cl_2 /n-hexane [M.pt.220°C].

Reaction of anhydrous stannous chloride with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato)dichloroditin (II), (XXXIV): It was obtained in the same manner as described above by taking the reagent N-trimethylsilyl-2-methylimidazole (0.77gm, 5.0 mmol) and stannous chloride (0.38 gm, 2.0 mmol) in THF. The reaction mixture was stirred for 2 hrs. It was also recrystallized from CH_2Cl_2 /n-hexane [M.pt.240°C, decomposes].

Reaction of bis(imidazolato)dibutyltin(IV) with triphenylphosphine; Isolation of bis(imidazolato)tin(II).triphenylphosphine, (XXXV): To the solution of (XXIX) (0.55 gm, 1.5 mmol) in 50 ml CH_2Cl_2 , triphenylphosphine (0.8 gm, 3.0 mmol) dissolved in 20 ml CH_2Cl_2 was added with vigorous stirring at room temperature for about 24 hrs. The reaction mixture was vacuum dried giving colourless crystalline mass which was washed several times with CH_2Cl_2 and ether to remove unreacted triphenylphosphine and dried in vacuo [M.pt.70°C].

Reaction of bis(2-methylimidazolato)dibutyltin(IV) with triphenylphosphine; Isolation of bis(2-methylimidazolato)tin(II).triphenylphosphine, (XXXVI): It was prepared in the same manner as above by dissolving bis(2-methylimidazolato)dibutyltin(IV) (0.79 gm, 2.0 mmol) in 25 ml CH_2Cl_2 and treating it with a solution of triphenylphosphine (1.04 gm, 4.0 mmol) with stirring in small portions at room temperature. The mixture was heated under reflux for Ca. 8 hrs under a slow stream of nitrogen. The solvent was removed under reduced pressure and the solid obtained was washed with an excess of hexane and then with ether, dried in vacuo. The crude was recrystallized from CH_2Cl_2 /n-hexane [M.pt.90°C].

Reaction of dimethyltin dichloride with N-trimethylsilylimidazole in presence of triphenylphosphine; Isolation of bis(imidazolato)tin(II).triphenylphosphine, (XXXV): Dimethyltin dichloride(0.4 gm, 2.0 mmol) dissolved in CH_2Cl_2 was reacted with N-trimethylsilylimidazole(0.56 gm, 4.0 mmol) in presence in presence of triphenylphosphine (0.52 gm, 2.0 mmol) with vigorous stirring at room temperature. The reaction mixture was then refluxed for Ca. 12 hrs. and then mixed with n-hexane yielding colourless solid. It was washed with ether to remove the impurities of the unreacted triphenylphosphine and the reagent then dried in vacuo [M.pt.70°C].

Reaction of dimethyltin dichloride with N-trimethylsilyl-2-methylimidazole in presence of triphenylphosphine; Isolation of bis(2-methylimidazolato)tin(II).triphenylphosphine, (XXXVI): The compound (XXXVI) was obtained when dimethyltin dichloride (0.4 gm, 2.0 mmol) dissolved in CH_2Cl_2 was treated with N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) in presence of triphenylphosphine (0.52 gm, 2.0 mmol) with vigorous stirring at room temperature. It was then refluxed for Ca. 10 hrs. and then n-hexane was added (20 ml) that resulted in the isolation of a colourless solid. Filtered and washed with ether and dried in vacuo. [M.pt. 90°C].

Reaction of bis(imidazolato)tin(II).triphenylphosphine with iodine; Isolation of diiodobis(imidazolato)tin(IV), (XXXVII): To a solution of bis(imidazolato)tin(II).triphenylphosphine (0.51 gm, 1.0 mmol) in CH_2Cl_2 (20 ml) was added iodine (0.25 gm, 1.0 mmol) with stirring at room temperature under a dry nitrogen atmosphere. The colour of the reaction mixture gradually changed from violet to red-orange indicating the oxidative addition of iodine to tin(II). After Ca. 1 hr. the reaction mixture was evaporated under reduced pressure and washed with hexane giving an orange solid [M.pt. 143°C]. The hexane washings were chromatographed on a SiO_2 column, elution with hexane provided triphenylphosphine in an approximately equivalent amount.

Reaction of bis(2-methylimidazolato)tin(II).triphenylphosphine with iodine; Isolation of diiodobis(2-methylimidazolato)tin(IV), (XXXVIII): The preparation of this compound was achieved by reacting equimolar amount of iodine(0.25 gm, 1.0 mmol) in 10 ml CH_2Cl_2 with a solution of compound (XXXIV) (0.54 gm, 1.0 mmol) in 20 ml CH_2Cl_2 in the same manner as above. The orange coloured solid thus obtained was filtered and washed with hexane and ether and dried in vacuo[M.pt.152°C]. The filtrate along with the washings was chromatographed on SiO_2 column, elution with hexane, here too, provided free triphenylphosphine.

Reaction of $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with trimethylsilylimidazole; Isolation of bis(imidazolato)bis(triphenylphosphine)zinc(II), (XXXIX): $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.3 gm, 2.0 mmol) was dissolved in THF (30 ml) and the reagent N-trimethylsilylimidazole (0.56 gm, 4.0 mmol) was added dropwise from a dropping funnel with continuous stirring. The reaction mixture was further stirred for almost 1 hr., colourless solid appeared in the solution. The reaction mixture was kept at low temperature for 24 hrs. The mother liquor was decanted in another flask leaving behind the colourless solid material. The mother liquor was mixed with 30 ml hexane, it also gave the white coloured crystalline mass. The solid was filtered, washed thoroughly with ether and n-hexane, dried in vacuo. [M.pt. 220°C].

Reaction of $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato) bis(triphenylphosphine)zinc(II), (XL): It was prepared in the same manner as described above for (XXXIX) by taking $[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.3 gm, 2.0 mmol) in 25 ml THF and treating it with the reagent N-trimethylsilyl-2-methylimidazole (0.61 gm, 4.0 mmol) with continuous stirring. The reaction mixture was kept at 5°C for 24 hrs. then mixed with 20 ml n-hexane for crystallization and kept at 5°C for 12 hrs. Colourless crystalline material obtained was washed with ether and dried in vacuo [M.pt. 230°C].

Reaction of $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-imidazole; Isolation of bis(imidazolato) cadmium(II), (XLI): $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.4 gm, 2.0 mmol) was taken in 30 ml THF, it was stirred for 15 mts. then the reagent N-trimethylsilylimidazole (0.56 gm, 4.0 mmol) mixed with 10 ml THF was continuously dropped to it. The reaction mixture was continuously stirred for 3 hrs., white coloured solid appeared in the solution. The solid was filtered off and filtrate was layered with hexane, it gave the second crop of the product. The solid was washed with hexane and ether and dried in vacuo. [M.pt. 100°C decomposes]. All the washings were collected and dried in vacuo giving white coloured shining crystalline material (1.0 gm) which has been identified as 2.0 mole equivalent of free $(\text{C}_6\text{H}_5)_3\text{P}$ [M.pt. 80°C].

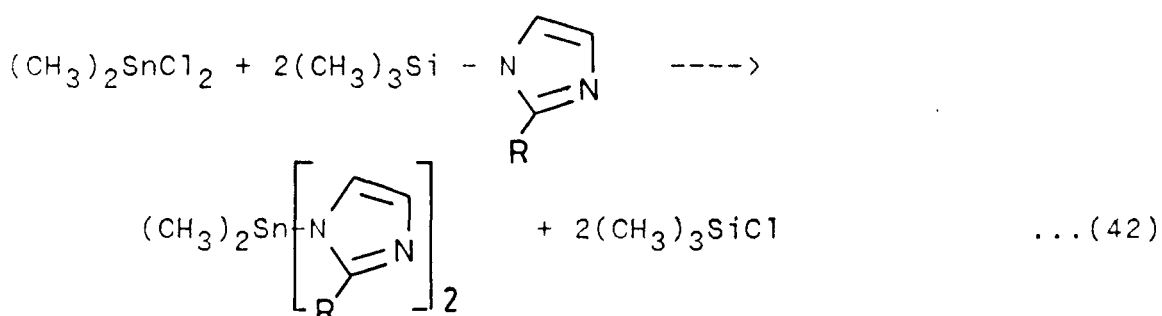
Reaction of $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato) cadmium(II), (XLII): $[\text{Cd}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.4 gm, 2.0 mmol) suspended in 30 ml THF was stirred for 15 mts. then the reagent N-trimethylsilyl-2-methylimidazole (0.61 gm, 44.0 mmol) was added to it in the manner described above for (XLI). The colourless solid was washed with ether and hexane and dried in vacuo [M.pt.115°C decomposes]. Filtrate alongwith the ether washings when dried in vacuo yield colourless shining crystalline material, (1.03 gm, Ca. 2.0 mole of $(\text{C}_6\text{H}_5)_3\text{P}$) it was identified as free $(\text{C}_6\text{H}_5)_3\text{P}$ from its melting point [80°C] i.r. and analytical data.

Reaction of $[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-imidazole; Isolation of bis(imidazolato) bis(triphenylphosphine)mercury(II), (XLIII): The synthesis of this compound was achieved by reacting $[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ (1.2 gm, 1.5 mmol) in 100 ml THF with the reagent N-trimethylsilylimidazole (0.43 gm, 3.0 mmol) with continuous stirring in an inert atmosphere. White turbidity was seen immediately after the addition of the reagent, stirred it for 2 hrs. resulting in a clear solution. This solution was vacuum dried giving a sticky oily yellowish white solid. It was washed with ether and dried. After drying the solid loses its stickiness [M.pt.228°C]. The mother liquor alongwith the washings were dried in vacuum and did not yield free triphenylphosphine even in traces.

Reaction of $[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2]$ with N-trimethylsilyl-2-methylimidazole; Isolation of bis(2-methylimidazolato) bis(triphenylphosphine)mercury(II), (XLIV): The synthesis of bis(2-methylimidazolato) bis(triphenylphosphine)mercury(II) was performed in the same manner as described above for (XLIII) by reacting dichlorobis(triphenylphosphine)mercury(II) (1.2 gm, 1.5 mmol) and N-trimethylsilyl-2-methylimidazole (0.46 gm, 3.0 mmol) in THF (100 ml). The colourless solid was obtained after prolong stirring [M.pt. 240°C]. In this case too, the washing and mother liquor when dried in vacuo did not yield liberated triphenylphosphine.

RESULTS AND DISCUSSION

Reaction of dimethyltin dichloride with N-trimethylsilylimidazole/2-methylimidazole; Isolation of bis(imidazolato)dimethyltin(IV), (XXVII) or bis(2-methylimidazolato)dimethyltin(IV), (XXVIII): For the reactions of dimethyltin dichloride with the reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole the product has been identified as the bis(imidazolato)-dimethyltin(IV), (XXVII) and bis 2-methylimidazolatotin(IV), (XXVIII). The results of the elemental analyses and stoichiometries of the products are shown in Table XII. Here too, the observed reactivity of the reagent(s) towards Sn-Cl bonds is apparently due to the affinity of the $(\text{CH}_3)_3\text{Si}$ group for chlorine resulting in the release of $(\text{CH}_3)_3\text{SiCl}$ similar to that observed for transition metal chlorides and their derivative complexes. The mode of reaction can be represented as shown by the following equation



R = H (XXVII)

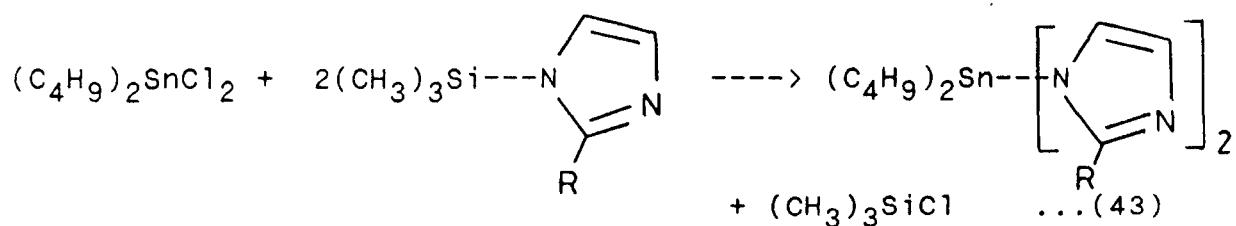
R = CH_3 (XXVIII)

The i.r. spectra of the compounds (Table-XIII) exhibit the characteristic^{42,89-94} imidazolate/2-methylimidazolate

ring vibrations in addition to the bands observed for the organic substituent i.e., CH_3 at their reported²¹⁹ positions. The appearance of a strong band at 535 cm^{-1} in the far i.r. region of the spectrum is assigned to the $\nu_{\text{asym}}(\text{Sn}^{\text{IV}}\text{-N})$ stretching frequency which is comparable to that reported²²⁰ in tetrakis (dimethylamido)tin(IV).

The compounds were soluble in usual organic solvents and behave as monomers in solution. The ^1H n.m.r. spectrum of the compounds (XXVII) and (XXVIII) (Table-XII) exhibited resonances characteristic of the imidazolate protons in addition to the signals arising from the proton of the organic substituent at the appropriate position.

Reaction of dibutyltin dichloride with the reagents N-trimethylsilylimidazole/2-methylimidazole; Isolation of bis(imidazolato)dibutyltin(IV), (XXIX) or bis(2-methylimidazolato)dibutyltin(IV), (XXX): The analytical results on the compounds obtained (Table-XII) agree well with the molecular formula as $[(\text{C}_4\text{H}_9)_2\text{SnL}_2]$ where L = imidazolate or 2-methylimidazolate moiety. Here too, all the chlorine has been replaced by the imidazolate moiety which has further been confirmed from the observed analytical data. The reaction seems to follow the following metathetic course as shown below:

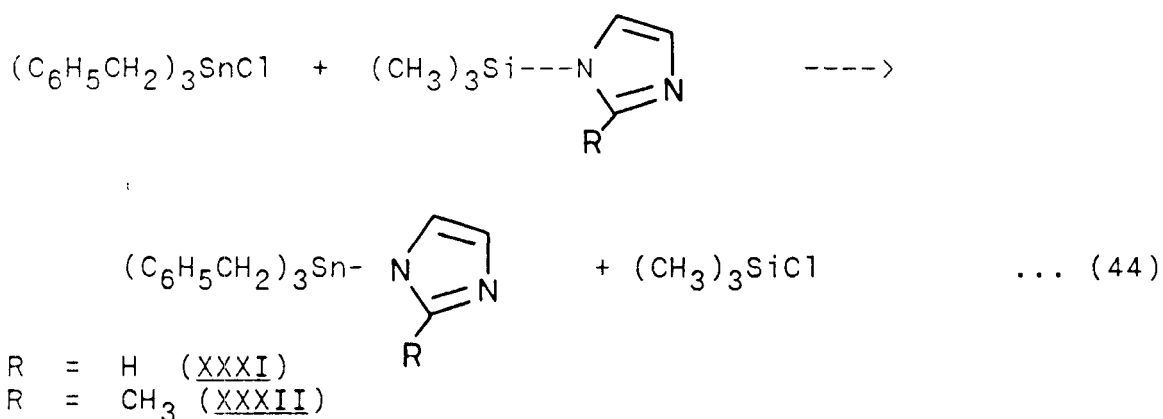


R = H (XXIX)

R = CH₃ (XXX)

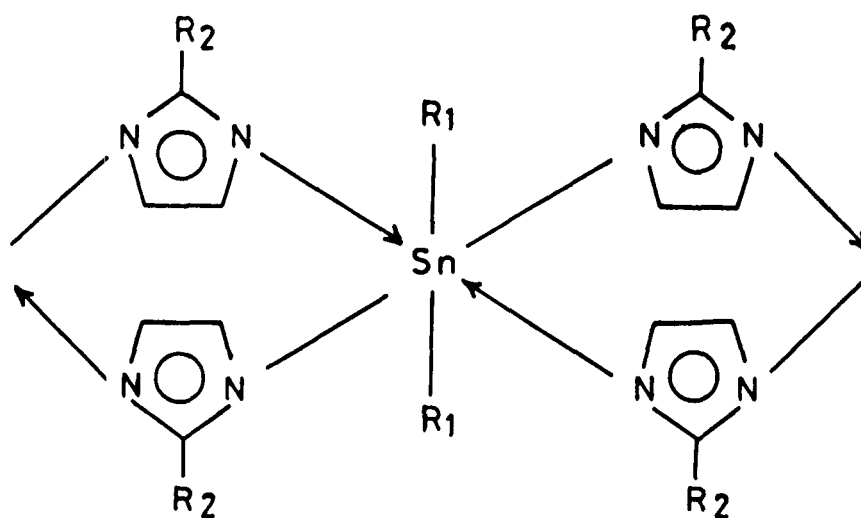
Both the compounds were soluble in most of the organic solvents, were low melting which indicated them to be monomeric in nature. The monomeric nature of the compounds was further confirmed by determining their molecular weights. The i.r. spectrum (Table-XII) of the compounds showed all the bands characteristic^{42,89-94} of the imidazolate ring stretching vibrations in the range 1600-1300 cm⁻¹ but slightly shifted (10-20 cm⁻¹) from their position that indicated in the free imidazole. The i.r. spectrum of the compounds (XXIX) and (XXX) also showed bands characteristic²¹⁹ of the butyl group. The strong band at 535 cm⁻¹ is assigned to the $\nu_{\text{asym}}(\text{Sn}^{\text{IV}}\text{-N})$ stretching vibration as reported²²⁰ by Bürger et. al. The ¹H n.m.r. spectrum of the compounds (XXIX) and (XXX) exhibited signals (Table-XII) arising from the imidazolate/2-methylimidazolate protons¹⁵⁴, including those arising from organic substituent at appropriate positions.

Reaction of tribenzyltinchloride with N-trimethylsilylimidazole/2-methylimidazole; Isolation of (imidazolato)tribenzyltin(IV), (XXXI) or (2-methylimidazolato)tribenzyltin(IV), (XXXII): The products that were obtained by the reaction of tribenzyltinchloride with the reagents (N-trimethylsilylimidazole/2-methylimidazole) were identified as $(C_6H_5CH_2)_3SnL$ (L =imidazolate or 2-methylimidazolate) from the results of elemental analyses suggesting the reaction to proceed through the following equation:



The i.r. spectrum of the compounds exhibited^{42,89-94} the characteristic imidazolato/2-methylimidazolato ring vibrations in addition to the strong bands arising from the organic substituent. A strong band that appeared in the region 530 cm^{-1} was assigned²²⁰ to the metal nitrogen band $\nu_{\text{asym}} (Sn^{IV} - N)$. The 1H n.m.r. spectrum (Table-XIII) of the compounds (XXXI), (XXXII) showed characteristic resonance arising from imidazolato/2-methylimidazolato protons as well as the resonance arising from the protons of organic substituent at their appropriate positions.

The lone pair at the imine nitrogen of the imidazole moiety may coordinate to the tin atom. However intramolecular coordination seems sterically improbable, the intermolecular coordination leading to an octahedral configuration for (XXVII), (XXVIII), (XXIX) and (XXX) as shown in figure-XXVIII while a trigonal bipyramidal geometry (Figure-XXIX) seems plausible for (XXXI) and (XXXII) in the condensed solid phase of these compounds. However, in solution of these compounds in non coordinating solvents, the intramolecular imine coordination would be weak suggesting a tetrahedral environment around Sn(IV) centre as the most reasonable molecular representation of these compounds.



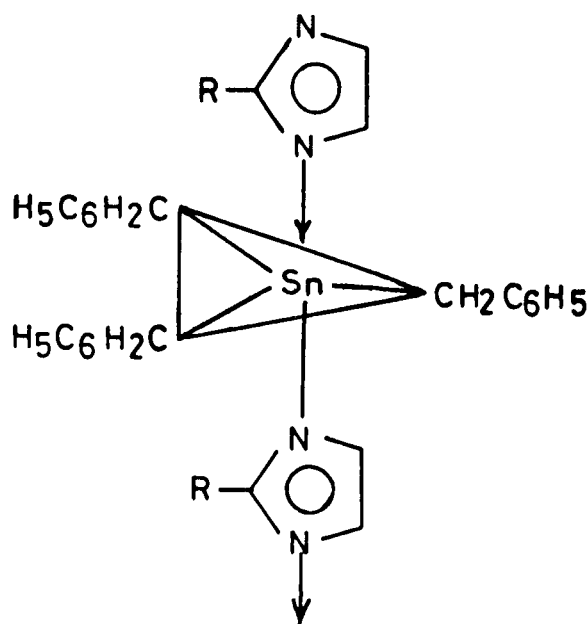
R₁ = CH₃ (XXVII), XXVIII)

R₁ = n - C₄H₉ (XXIX, XXX)

R₂ = H (XXVII, XXIX)

R₂ = CH₃ (XXVIII, XXX)

(Figure-XXVIII)



R = H (XXXI)

R = CH₃ (XXXII)

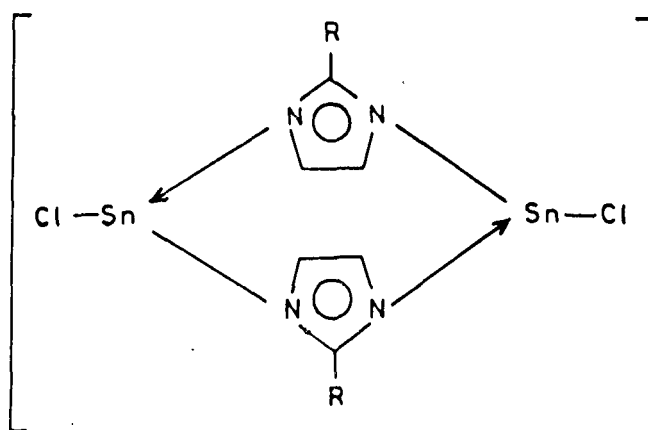
(Figure - XXIX)

Reaction of anhydrous stannous chloride with N-trimethylsilylimidazole/2-methylimidazole; Isolation of bis(imidazolato)dichloroditin(II), (XXXIII) or bis(2-methylimidazolato)dichloroditin(II), (XXXIV): The stoichiometry of the product of the reaction of the anhydrous stannous chloride with the reagents N-trimethylsilylimidazole/2-methylimidazole is compatible with the formula as [SnClL]₂. There is one chlorine always retained in molecular unit, even though, a slight excess of the reagents were used to ensure total removal of the chlorines as (CH₃)₃SiCl. A similar observation has also been reported²²¹ for the reaction of SnCl₂ with E(t-Bu)₂SiMe₃ (E=P, As). The compounds (XXXIII) and (XXXIV) were high melting (above

200°C) and did not dissolve in usual organic solvents excepting DMSO. Molecular weight (Table-XII) measurements indicated them to be dimers. In the i.r. spectra of the compounds imidazolate/2-methylimidazolate ring vibrations appeared at the expected^{42,89-94} positions. A band of medium intensity at 410 cm⁻¹ has been assigned to ν (Sn^{II}-N) stretching vibration²²² which seems reasonable in view of the report¹⁶⁷ that Cd-N bond frequency in Cd[N(Si/CH₃)₃]₂ also appears in this range. The position of the Sn^{II}-N bond frequency is lower than that of the Sn^{IV}-N bond. This observation is parallel to that reported²⁰⁷ for the corresponding Sn-O i.e., (Sn^{IV}-O) bond stretching frequency lies at higher position than that arising from Sn^{II}-O bond. This may be rationalized in terms of the presence of substantial polarity expected for the Sn^{II}-N bond, which is compatible with the observed medium intensity of this vibration. The ν (M-Cl) stretching vibration for the compounds (XXXIII) and (XXXIV) appeared at the reported²²³ position (Table-XIII) of terminal ν (Sn-Cl) stretching vibration.

The dimers (XXXIII) and (XXXIV) did not exhibit any tendency to transform into the monomeric adduct like [SnClL.Base] as was indicated by the following observations. Treatment of (XXXIII) and (XXXIV) with strong bases like pyridine, pyridine-N-oxide(PyNO), pipyridine and even Bu₄NI did not indicate any apparent reaction rather unchanged

reactants were obtained (identified by physico-chemical methods). In order to probe further this behaviour of the complexes, it was thought to use a well known monomeric tin(II) chloride complex $[\text{SnCl}_2 \cdot \text{PyNO}]$ (1:1 adduct) as precursor for the reaction with the reagents *N*-trimethylsilylimidazole/2-methylimidazole with the hope of isolating a monomeric species. It also afforded the products (XXXIII) and (XXXIV) respectively with the recovery of an equivalent amount of free PyNO. This behaviour is apparently in contrast to the findings reported for bis(dimethylamido) tin(II)²²² and tin(II) diolate²²⁴ dimers which have been shown to produce 1:1 adducts with bases such as bipyridine, phenanthroline and result the ionic complexes when reacted with Bu_4NI . This unusual behaviour of (XXXIII) and (XXXIV) may be rationalized in terms of the strong bridging capability provided by the pyridyl (imine)nitrogen of the imidazolate/2-methylimidazolate moiety towards Sn(II) centre resulting in an intact dimer as shown below:



R = H (XXXIII)
 R = CH_3 (XXXIV)

(Figure - XXX)

Reaction of bis(imidazolato)dibutyltin(IV) and bis(2-methylimidazolato)dibutyltin(IV) with triphenylphosphine and that of dimethyltin dichloride with N-trimethylsilyl-imidazole/-2-methylimidazole in presence of equivalent amount of triphenylphosphine; Isolation of bis(imidazolato) tin(II). triphenylphosphine, (XXXV) or bis(2-methylimidazolato) tin(II) triphenylphosphine, (XXXVI): The reaction of bis(imidazolato)dibutyltin(IV) or bis(2-methylimidazolato)dibutyltin(IV) with an excess of triphenylphosphine (vide-supra experimental part) at the reflux temperature of CH_2Cl_2 under an inert atmosphere has proceeded with cleavage of the Sn-C bond to form the adduct $[\text{SnL}_2(\text{C}_6\text{H}_5)_3\text{P}]$ [L = imidazolate, (XXXV); L = 2-methylimidazolate, (XXXVI)] in Ca. 50% yield. The absence of butyl group in the products (XXXV) and (XXXVI) was confirmed from the spectral data i.e. ^1H n.m.r. spectrum (Table-XIII) did not show characteristic butyl resonances rather exhibited well resolved signals characteristic of the imidazolate (7.3 δ and 7.45 δ) and coordinated triphenylphosphine (7.6 - 7.85 δ) protons, while the i.r. spectrum (Table-XIII) showed no characteristic butyl bands. The ^{31}P n.m.r. spectrum of (XXXV) and (XXXVI) contained a sharp singlet at 4.3 ppm which is in the range reported²²⁵ for $(\text{C}_6\text{H}_5)_3\text{P}$ coordinated to metal ions.

The product obtained from the direct reaction of dimethyltin dichloride with the reagents N-trimethyl-

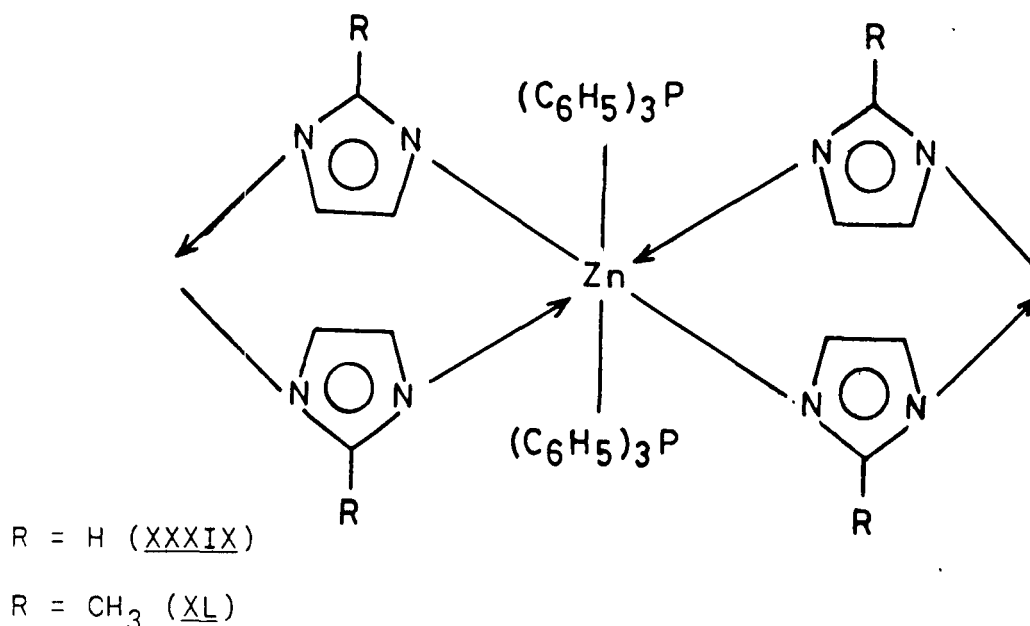
silylimidazole/2-methylimidazole in presence of triphenylphosphine were found to have the stoichiometry comparable to (XXXV) or (XXXVI). Here, too, the cleavage of Sn-C bond has produced the adduct $[\text{SnL}_2 \cdot (\text{C}_6\text{H}_5)_3\text{P}]$ i.e (XXXV) or (XXXVI). It was further confirmed from its i.r and ^1H n.m.r. spectral data. ^1H n.m.r. (Table-XIII) spectrum of both the compounds did not show resonance characteristic of alkyl group instead the resonances characteristic of imidazolate ring protons and that of the coordinated triphenylphosphine are observed at their appropriate position. The i.r. spectrum of (XXXV) and (XXXVI) did not show bands characteristic of alkyl group rather bands of coordinated triphenylphosphine are seen at their expected positions. Infra-red spectrum of both the complex i.e. (XXXV) and (XXXVI) contained characteristic imidazolate ring vibrations^{42,89-94} and a band of medium intensity in the far-i.r. region, at 418 cm^{-1} , characteristic²²² of the $\nu_{\text{asym}}(\text{Sn}^{\text{II}}-\text{N})$ stretching vibration.

The cleavage of Sn-C bond in organotin (IV) derivatives is not a very common feature, however there are a few reports^{226,227} that reagents such as PX_3 ($\text{X}=\text{halogen}$), AsCl_3 and BiCl_3 show similar behaviour.

Reaction of bis(imidazolato)tin(II).triphenylphosphine with I_2 ; Isolation of diiodobis(imidazolato)tin(IV), (XXXVII) or that of bis(2-methylimidazolato)tin(II).triphenylphosphine

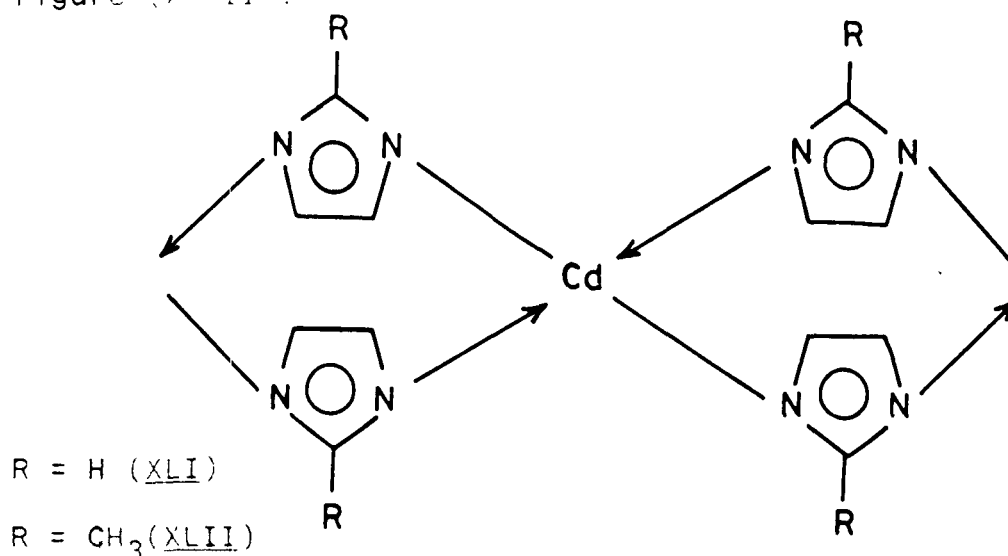
with I_2 ; Isolation of diiodobis(2-methylimidazolato)tin (IV), (XXXVIII): In order to ascertain the stoichiometry of the formation of (XXXV) and (XXXVI) and to obtain chemical evidence for the oxidation state of the tin atom in the molecule, (XXXV) and (XXXVI) were subjected to an oxidative addition reaction using an equivalent amount of iodine. A sharp change in the colour of iodine was observed and the reaction mixture finally afforded orange microcrystalline products (XXXVII) and (XXXVIII) respectively along with equivalent amount of free triphenylphosphine (Experimental Section). Analytical data of the compounds (XXXVII) and (XXXVIII) agree well with the stoichiometry as $[SnI_2L_2]$ [L =imidazolate (XXXVII), 2-methylimidazolate (XXXVIII)]. A comparison of the spectral data of (XXXVII) and (XXXVIII) with the corresponding analogues (XXXV) and (XXXVI) confirmed the complete liberation of triphenylphosphine during the course of formation of (XXXVII) and (XXXVIII). These observations indicate that compounds (XXXV) and (XXXVI) are genuine tin(II) compounds and that the reaction of (XXIX) and (XXX) with excess of triphenylphosphine in refluxing CH_2Cl_2 and that of the dimethyltin dichloride with the reagents *N*-trimethylsilylimidazole/2-methylimidazole in presence of triphenylphosphine in CH_2Cl_2 proceeds through a redox step which may be initiated either by triphenylphosphine or CH_2Cl_2 or both.

vibrations of the imidazolate/2-methylimidazolate moiety overlap with those arising from triphenylphosphine, nevertheless they can be identified on comparing with the already reported¹⁵⁴ i.r. spectrum of the reagent(s). The appearance of a single band of medium intensity at about 400 cm^{-1} is, unequivocally, assignable¹⁶⁴ to ν M-N stretching vibration. It is well known²²⁸ that M-N stretching vibrations are often sensitive to the environment around Zn(II), Cd(II) or Hg(II) ion i.e. appear as a broad single band in pseudo-octahedral environment but split into at least two bands when the environment around metal is pseudo-tetrahedral with C_{2v} symmetry. The compounds (XXXIX) and (XL) may best be represented as having octahedral geometry involving imidazolate bridging as shown below in figure-XXXI.



(Figure-XXXI)

the ν (M-N) stretching vibration region¹⁶⁷ (Table-XV) corroborates the pseudo-tetrahedral geometry²²⁸ of the compound with a probable C_{2v} symmetry of the molecule. The splitting of M-N vibration band reported⁴² to occur for the cobalt(II) pyrazole complexes in the form of a shoulder in the main band has been assigned to be due to a site symmetry lower than octahedral, of course, preferably C_{2v} (tetrahedral) which has also been observed in many other cases. The molecular presentation of $[CdL_2]$ may be given as shown in figure (XXXII).



(Figure-XXXII)

Reaction of $[Hg\{(C_6H_5)_3P\}_2Cl_2]$ with the reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole; Isolation of bis(imidazolato)bis(triphenylphosphine)mercury(II), (XLIII) and bis(2-methylimidazolato) bis(triphenylphosphine)mercury(II), (XLIV): The analytical data (Table-XIV) of the products obtained from the title reaction agree well with the formula of the compound as

TABLE-XII
Analytical data of complexes.

Complexes		% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% M Found (Calcd.)	Mol. Wt. Found (Calcd.)
$[\text{CH}_3)_2\text{Sn}(\text{Iz})_2]$	(XXVII)	33.9 (34.0)	4.2 (4.3)	19.7 (19.8)	41.9 (42.0)	290 (283)
$[\text{CH}_3)_2\text{Sn}(\text{MeIz})_2]$	(XXVIII)	38.5 (38.6)	5.0 (5.2)	17.9 (18.0)	38.0 (38.2)	302 (311)
$[(\text{C}_4\text{H}_9)_2\text{Sn}(\text{Iz})_2]$	(XXIX)	45.8 (45.8)	6.5 (6.6)	15.2 (15.3)	32.2 (32.3)	361 (367)
$[(\text{C}_4\text{H}_9)_2\text{Sn}(\text{MeIz})_2]$	(XXX)	48.4 (48.6)	6.9 (7.1)	14.1 (14.2)	29.4 (30.0)	387 (395)
$[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{Iz})]$	(XXXI)	62.5 (62.8)	5.1 (5.3)	6.0 (6.1)	25.7 (25.8)	448 (459)
$[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{MeIz})]$	(XXXII)	63.2 (63.5)	5.5 (5.5)	5.8 (5.9)	24.0 (25.1)	467 (473)
$[\text{SnCl}(\text{Iz})_2]$	(XXXIII)	16.2 (16.3)	1.3 (1.4)	12.6 (12.7)	53.5 (53.6)	455 (442)
$[\text{SnCl}(\text{MeIz})_2]$	(XXXIV)	20.4 (20.4)	2.0 (2.1)	11.7 (11.9)	49.6 (50.4)	461 (470)
$[\text{Sn}(\text{Iz})_2 \cdot (\text{C}_6\text{H}_5)_3\text{P}]$	(XXXV)	55.9 (56.0)	4.1 (3.1)	10.8 (10.8)	22.9 (23.0)	525 (515)
$[\text{Sn}(\text{MeIz})_2 \cdot (\text{C}_6\text{H}_5)_3\text{P}]$	(XXXVI)	57.2 (57.5)	4.4 (4.6)	10.3 (10.3)	21.0 (21.8)	535 (543)
$[\text{SnI}_2(\text{Iz})_2]$	(XXXVII)	14.3 (14.2)	1.3 (1.2)	11.8 (11.1)	24.1 (23.4)	500 (506)
$[\text{SnI}_2(\text{MeIz})_2]$	(XXXVIII)	17.6 (18.0)	2.0 (2.0)	10.3 (10.5)	21.7 (22.2)	522 (534)

TABLE-XIII

Imidazolate ring, M-N, M-Cl/M-P frequencies (cm^{-1}) observed in the i.r.* spectra and $^1\text{Hn.m.r.}^*$ spectral data of complexes.

Complexes	Imidazolate ring vibration				$\nu(\text{M-N})$	$\nu(\text{M-Cl})/\nu(\text{M-P})$	$\delta\text{H}(60\text{MHz})$ imidazolate/ 2-methylimidazo- late protons	
	R ₁	R ₂	R ₃	R ₄				
$[(\text{CH}_3)_2\text{Sn}(\text{Iz})_2]$	(XXVII)	1590s	1490m	1410m	1320w	535s	-	7.31 (1H), 7.50 (2H)
$[(\text{CH}_3)_2\text{Sn}(\text{MeIz})_2]$	(XXVIII)	1585s	1480m	1420s	1320m	535s	-	2.35 (3H), 6.8 (2H)
$[(\text{C}_4\text{H}_9)_2\text{Sn}(\text{Iz})_2]$	(XXIX)	1600s	1480m	1420s	1310m	530s	-	7.29 (1H), 7.48 (2H)
$[(\text{C}_4\text{H}_9)_2\text{Sn}(\text{MeIz})_2]$	(XXX)	1610s	1475m	1425m	1320s	535s	-	2.46 (3H), 7.08 (2H)
$[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{Iz})]$	(XXXI)	1585s	1485m	1420m	1320m	535s	-	7.24 (1H), 7.61 (2H)
$[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{MeIz})]$	(XXXII)	1580s	1480m	1425m	1325m	530s	-	2.45 (3H), 6.8 (2H)
$[\text{SnCl}(\text{Iz})_2]$	(XXXIII)	1620m	1480m	1420m	1320s	410m	290m	7.32 (1H), 7.55 (2H)
$[\text{SnCl}(\text{MeIz})_2]$	(XXXIV)	1600m	1480m	1425m	1320s	410m	295m	2.26 (3H), 7.0 (2H)
$[\text{Sn}(\text{Iz})_2 \cdot (\text{C}_6\text{H}_5)_3\text{P}]$	(XXXV)	1595s	1475m	1425m	1320s	415m	315w	7.30 (1H), 7.45 (2H)
$[\text{Sn}(\text{MeIz})_2 \cdot (\text{C}_6\text{H}_5)_3\text{P}]$	(XXXVI)	1600m	1480s	1425m	1320s	410m	315w	2.40(3H), 7.29 (2H)
$[\text{SnI}_2 \cdot (\text{Iz})_2]$	(XXXVII)	1605s	1485m	1425s	1330s	510s	-	7.25 (1H), 7.55 (2H)
$[\text{SnI}_2 \cdot (\text{MeIz})_2]$	(XXXVIII)	1620m	1480m	1420m	1330s	530s	-	2.46 (1H), 7.1 (2H)

* i.r. stretching frequencies and proton resonances of $(\text{C}_6\text{H}_5)_3\text{P}$ and the alkyl substituent on the tin atom are omitted.

TABLE-XIV

Analytical data of complexes

Complexes		% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% M Found (Calcd.)
$[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{Iz})_2]_x$	(<u>XXXIX</u>)	68.9 (69.7)	4.7 (4.9)	7.5 (7.7)	8.4 (9.0)
$[\text{Zn}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{MeIz})_2]_x$	(<u>XL</u>)	70.0 (70.3)	5.0 (5.3)	7.2 (7.5)	8.2 (8.8)
$[\text{Cd}(\text{Iz})_2]$	(<u>XLI</u>)	28.9 (29.2)	2.2 (2.5)	22.3 (22.7)	44.6 (45.6)
$[\text{Cd}(\text{MeIz})_2]$	(<u>XLII</u>)	34.6 (35.0)	3.4 (3.7)	20.4 (20.4)	40.2 (40.9)
$[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{Iz})_2]$	(<u>XLIII</u>)	58.6 (58.7)	4.2 (4.2)	6.4 (6.5)	23.0 (23.4)
$[\text{Hg}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{MeIz})_2]$	(<u>XLIV</u>)	59.3 (59.6)	4.4 (4.5)	6.3 (6.3)	22.1 (22.6)

TABLE-XV

Imidazolate and $(C_6H_5)_3P$ -ring, $M-N$ stretching frequencies (cm^{-1}) observed in the i.r. spectra; ^{31}P n.m.r. spectral data of complexes.

Complexes	Imidazolate ring vibration				$(C_6H_5)_3P$	M-N	^{31}P n.m.r. (61.7 MHz) $\delta(C_6H_5)_3P$ ppm.
	R ₁	R ₂	R ₃	R ₄			
$[Zn\{(C_6H_5)_3P\}_2(Iz)_2]$ (XXXIX)	1570m	1480s	1435s	1310m	1480s, 1430s, 1100s, 750s, 700s, 510s	400m	28.5
$[Zn\{(C_6H_5)_3P\}_2(MeIz)_2]$ (XLI)	1580m	1480s	1430s	1320m	1480s, 1430s, 1090s, 740s, 700s, 535s, 505m	410m	28.0
$[Cd(Iz)_2]$ (XL)	1580m	1480m	1420m	1320s	-	400m 390m	-
$[Cd(MeIz)_2]$ (XLII)	1600m	1470m	1425m	1320s	-	400m 390w	-
$[Hg\{(C_6H_5)_3P\}_2(Iz)_2]$ (XLIII)	1600m	1485s	1450s	1320m	1485, 1450s, 1100s, 760s, 700s, 500s	400m	17.0
$[Hg\{(C_6H_5)_3P\}_2(MeIz)_2]$ (XLIV)	1590m	1480s	1430s	1330m	1480s, 1430s, 1090s, 750s, 700s, 510s	405m	17.5

CHAPTER-VI

LIGATING CHARACTERISTIC OF A LABILE P(III)
DERIVATIVE $RP(NCS)_2$ ($R=CH_3$ OR C_6H_5) TOWARDS A
FEW TRANSITION METAL IONS

INTRODUCTION

Organic isothiocyanates RNCS ($\text{R}=\text{alkyl, aryl or acyl}$) are versatile Lewis bases and their coordination chemistry has been thoroughly investigated ^{103,104}. They behave as ambidentate ligands providing different coordination sites to metal ions. The chemistry of derivatives like $\text{R}_n\text{E}(\text{NCS})_{3-n}$ ($\text{R}=\text{CH}_3$, C_6H_5 or C_6F_5 and $\text{E}=\text{P}$ or As) where the NCS group is bonded to a non-metal atom other than carbon, especially the group-XV elements in the periodic table, is scarcely described in the literature. However, a few members of this class of compounds have been known^{229,230} for quite a long time. Organophosphorus isothiocyanates $\text{RP}(\text{NCS})_2$ and $(\text{OR})\text{P}(\text{NCS})_2$ are reported^{110,230,231} to form in non-polar solvents from reaction of the appropriate halophosphine with a thiocyanating agent. However, former class of compounds invariably decompose if isolation from solvent is attempted²³⁰. The low stability of $\text{RP}(\text{NCS})_2$ may be one of the possible contributing factors to the lack of interest shown in the study of their reactivity towards metallic substrates. It has, recently, been reported²³² that stabilization of an unstable phospho-alkyne can be achieved by complex formation with a metal. It is thus likely that the fragile elemento-organic moiety like $-\text{P}(\text{NCS})_2$ possessing electron rich centres can be stabilized through coordination to metals. This chapter describes the investigations of the reactivity of the

elusive phosphorus(III) derivatives $\text{RP}(\text{NCS})_2$ ($\text{R}=\text{CH}_3$ or C_6H_5) towards transition metal ions and the isolation of stable complexes in which the $-\text{P}(\text{NCS})_2$ moiety is stabilized via coordination through its P and or S atoms.

EXPERIMENTAL

Reagents used:

The hydrated metal chlorides e.g. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Glaxo-India), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (E. Merck) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (s.d. Fine Chem. Ltd.) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (BDH, England) were commercially pure samples and dehydrated before use while VCl_3 (BDH, England), FeCl_3 (s.d. Fine Chem. Pvt. Ltd.), CH_3PCl_2 (Aldrich) $\text{C}_6\text{H}_5\text{PCl}_2$ (Aldrich) were used as received. AgSCN was prepared according to established method²³³ by the use of KNCS (E. Merck) and AgNO_3 (Glaxo-India). Acetic anhydride, dichlormethane, Ether, n-hexane were dried before use.

PREPARATION OF THE PRECURSORS:

Dehydration of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ¹⁵⁸: Hydrated managnese chloride was stirred in excess acetic anhydride for 30 mts. and then refluxed for about 4 hrs. The solid was filtered off and dried under vacuo. Then it was washed thoroughly with ether till the pungent smell of acetic anhydride ceases to come.

Preparation of silver thiocyanate²³³: A solution of AgNO_3 (1.69 gm, 10.0 mmol) in distilled water was treated with the stoichiometric amount of KNCS (0.97 gm, 10.0 mmol). The precipitate formed was filtered, washed and dried in vacuo at 70 °C.

Preparation of methyldiisothiocyanatophosphine, $\text{CH}_3\text{P}(\text{NCS})_2$:

An excess of silver thiocyanate (2.48 gm, 15.0 mmol) was reacted with CH_3PCl_2 (0.58 gm, 5.0 mmol) with continuous stirring in 20 ml CH_2Cl_2 . It was stirred for 2 hrs. at room temperature under a dry nitrogen atmosphere. The excess of AgSCN and AgCl byproduct were removed by filtration in a closed system through a sintered glass frit. The colour of the solution was light pinkish yellow. Evaporation of the solvent under reduced pressure has provided a reddish brown oil which after spectral and micro analyses was found to contain decomposed products (Please see Results and Discussion).

Preparation of phenyldiisothiocyanatophosphine, $\text{C}_6\text{H}_5\text{P}(\text{NCS})_2$:

Dichlorophenylphosphine (0.9 gm, 5.0 mmol) taken in 5 ml CH_2Cl_2 was added to a solution of silver thiocyanate (2.4 gm, 5.0 mmol) in 15 ml CH_2Cl_2 with continuous stirring at room temperature. The reaction mixture was allowed to stir for Ca. 2 hrs. to ensure the completion of the reaction. It was then filtered off to remove the unreacted AgSCN and byproduct AgCl impurities. The removal of solvent yielded a dark red coloured oil which was found to contain the decomposed products.

PREPARATION OF THE COMPLEXES:

Reactivity of methyldiisothiocyanatophosphine and of phenyldiisothiocyanatophosphine towards anhydrous metal

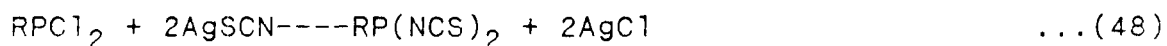
chlorides; Isolation of stable transition metal complexes of the type $[M(L)Cl]Cl$, [Where $M = Mn$ (XLV), (XLVI); Co , (XLVII), (XLVIII); Ni (XLIX), (L); Cu (LI), (LII) and $L = CH_3P(NCS)_2$ or $C_6H_5P(NCS)_2$] and $[M(L)Cl]Cl_2$ [Where $M = Fe$ (LIII), (LIV); V (LV), (LVI) and $L = CH_3P(NCS)_2$ or $C_6H_5P(NCS)_2$] and $[Cu(L)_2Cl]$ [where $L = CH_3P(NCS)_2$ (LVII) or $C_6H_5P(NCS)_2$ (LVIII)]: As both the ligands exhibited the tendency to decompose in the absence of the solvent, it was decided to use in-situ condition to examine their reactivity towards anhydrous metal chlorides viz. VCl_3 , $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $CuCl$. The reaction procedure adopted and the isolation of the final products for the individual reactions were almost identical, it is therefore, worthwhile to describe only the general procedure as below:

A freshly prepared solution of the ligand (Ca. 5.0 mmol) in CH_2Cl_2 was directly filtered to a vigorously stirred suspension of the equimolar amount of the metal salt in the same solvent (Ca. 30-40 ml) in a closed system with dry N_2 atmosphere at room temperature. Sharp colour change in some of the cases were observed and the reaction mixture was stirred for Ca. 2-3 hrs. It was decanted to remove unreacted metal salt from the mother liquor which was concentrated by vacuum evaporation and mixed with Ca. 30-40 ml of n-hexane, kept at $5^\circ C$ for about 1 or 2 day(s) yielding stable solid compounds which have been filtered, washed and dried in vacuo. The compounds were fairly stable in air. The colour

and melting points for the individual complexes have been illustrated in Table-XVII.

RESULTS AND DISCUSSION

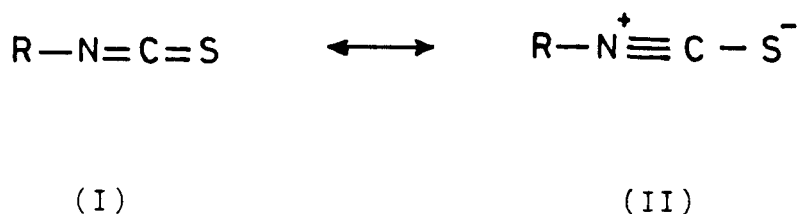
The reaction of RPCl_2 ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) with AgSCN is, apparently a metathetic exchange i.e.



$\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$.

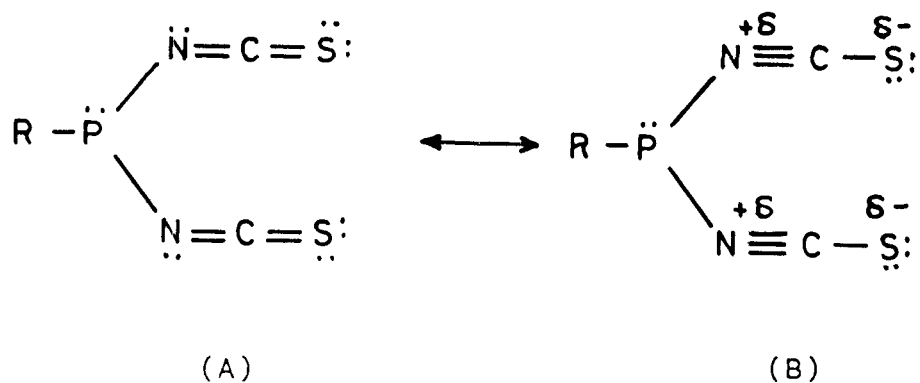
The complete conversion of the substrate RPCl_2 ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) into diisothiocyanate analogue has been ascertained by monitoring the i.r. spectrum of the reaction mixture at stages. The complete disappearance of the characteristic $\nu(\text{P-Cl})$ stretching vibration at 520 cm^{-1} with the concomitant appearance of new band at 1160 cm^{-1} assignable to $\nu(\text{P-N})$ stretching vibration¹³⁴ in addition to other characteristic^{103,110,230,231} ν_{asym} and ν_{sym} NCS vibrations (Table-XVI) indicate the complete conversion into the product $\text{CH}_3\text{P(NCS)}_2$ or $\text{C}_6\text{H}_5\text{P(NCS)}_2$ without any trace of unreacted substrate in the reaction mixture. Thiocyanate group if bonded through S atom to the organic substituent as R-SCN are termed as organic thiocyanates or normal thiocyanates. The characteristic i.r. frequencies for such linkage is reported to be exhibited at $2150\text{--}2200$ and $670\text{--}700 \text{ cm}^{-1}$ assigned as pseudo-antisymmetric and symmetric NCS stretching vibration. However, if bonding is through N atom it has been named as isothiocyanates (R-NCS). In organic isothiocyanates (RNCS) the three important stretching modes which could be expected to appear⁹⁹ are the R-N stretch, the N-C stretch and C-S

stretch. These three modes would be expected to interact and mix with each other because of the extensive N-C-S π -system and because of the similarity in energy. In particular, the N-C stretch and C-S stretch are known to be highly mixed and indeed have been labelled as NCS asymmetric stretch, $\nu_{\text{asym}}(\text{NCS})$ and NCS symmetric stretch, $\nu_{\text{sym}}(\text{NCS})$ vibration respectively. The free organoisonothiocyanate ligands exhibit the $\nu_{\text{asym}}(\text{NCS})$ in 2300-2000 cm^{-1} region and the $\nu_{\text{sym}}(\text{NCS})$ in 900 cm^{-1} region prepondering with the canonical space structures (shown below) in which structure (II) predominates⁹⁹ i.e.



(Figure-XXXIII)

In the present moiety i.e RP (NCS)₂ too, the $\nu_{\text{asym}}(\text{NCS})$ and $\nu_{\text{sym}}(\text{NCS})$ vibrations are indicated at 2040 and 960 cm^{-1} respectively (Table-XVI) confirming the predominance of the canonical structure B out of the two possible resonating forms i.e.



(Figure-XXXIV)

Furthermore, the i.r. spectrum of the ligand solution did not show any band in $1300-1350 \text{ cm}^{-1}$ region characteristic of $\nu(\text{P}=\text{N})$ stretching vibration¹³⁴. This reveals that the lone pair on phosphorus atoms is apparently lying free which may be rationalized in terms of its directional nature (sp^3 hybrid) and is in apt to dilute the positive charge on nitrogens i.e. it does not interact with the NCS bonding and the positive charge on nitrogen remains localized as in structure B.(Figure-XXXIV).

Moreover, it is well known that N-C-S has a tendency to adopt a linear skeleton. In isothiocyanates, linkage is through nitrogen of the NCS moiety. In the present $\text{RP}(\text{NCS})_2$ system, considering the molecular model, phosphorus (sp^3 hybrid) is covalently bonded to NCS through nitrogen in the way that it is not co-linear with NCS skeleton rather

makes an angle less than 180° similar to that reported²³⁴ for HNCS system where hydrogen atom is always bent from the rest NCS bonding.

The effort to isolate the ligands $\text{RP}(\text{NCS})_2$ in neat form i.e. free from the solvent through vacuum evaporation of the solvent from the reaction mixture has resulted in a dark reddish brown syrupy oil. The results of the elemental analyses of the oil did neither provide reproducible data nor were in agreement with the expected stoichiometry of the product $\text{RP}(\text{NCS})_2$. The i.r. spectrum of the neat oil showed a number of new bands in addition to those indicated in Table-XVI. The additional bands at 1270 and 760 cm^{-1} can be attributed to $\nu(\text{P=O})$ and $\nu(\text{P=S})$ stretching vibrations^{110,230,231} respectively. This indicates that $\text{RP}(\text{NCS})_2$ is unstable in the absence of the solvent and decomposes into corresponding phosphoryl and thiophosphoryl species. The precise composition of the decomposition product(s) has not been determined. This behaviour of $\text{RP}(\text{NCS})_2$ is in contrast to that of the corresponding $(\text{RO})\text{P}(\text{NCS})_2$ which is known to be fairly stable under normal conditions.²³⁵ The extra stability of the latter system may reasonably be accounted for an additional overlap between the filled non-bonding $p\pi$ -orbital of oxygen and the empty low lying $d\pi$ -orbital on phosphorus. This additional (P-OR) π bond overlap in phosphorus (V) derivatives is known to

influence their reactivity²³⁶ towards nucleophiles. The absence of similar π -overlap in $\text{RP}(\text{NCS})_2$ may have a stabilizing effect. However, the fragile $\text{RP}(\text{NCS})_2$ ($\text{R}=\text{CH}_3, \text{C}_6\text{H}_5$) shows considerable reactivity towards transition metal ions, affording stable microcrystalline solid compounds.

The color, melting point and results of elemental analyses of the solid compounds obtained from the reaction of the ligands $\text{RP}(\text{NCS})_2$ with metal chlorides are shown in Table-XVII. These are monomeric in nature behaving as 1:1 electrolytes except for (LVII) and (LVIII) [which are non electrolyte] and (LIII), (LIV), (LV), (LVI) [1:2 electrolyte] in DMSO²³⁷.

The important bands observed in the i.r. spectra of the compounds have been summarized in Table-XVI. It is evident that the position of the characteristic ν_{asym} and $\nu_{\text{sym}}^{\text{NCS}}$ frequencies do not change significantly after complexation from that in the free ligand. The N-C-S bonding may provide the following three possible modes of coordination to metal ions. Coordination through nitrogen atom, would result in a decrease in the bond order between carbon and nitrogen atom indicating predominance of structure A (Figure-XXXIV) in complexes. This effect would be reflected by a large negative shift in the $\nu_{\text{asym}}(\text{NCS})$ stretching frequency compared to that in the free ligand. However, coordination through S atom of NCS group will

maintain the predominance of structure B, consequently, $\nu_{\text{asym}}(\text{NCS})$ frequency will remain unaffected. Coordination involving the C-S bond similar to that reported¹⁰⁴ by Baireid and Wilkinson in $[\text{Rh}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{PhPNCS})_2\text{Cl}]$ and $[\text{Pt}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{PhPNCS})]$ may also be envisaged. The characteristic NCS frequencies for such mode have been shown to lie in the range 1700-1600 and 850-750 cm^{-1} for asymmetric and symmetric NCS vibrations respectively.

In view of the observation that the characteristic position of NCS frequencies do not change significantly from that observed in the uncomplexed ligand (Table XVI) it can unequivocally be preponed that in the present complexes coordination is through the sulphur atom. Sulphur atom a class(b) on Pearson's scale²³⁸, is considered a good donor site for class(b) metals. In the present complexes, the observed extra basicity of S atom in comparison to N atom in the $-\text{P}(\text{NCS})_2$ moiety with class(a) metals is probably, the result of the additional free lone pair at sulphur. The lone pair at nitrogen is partially used in bonding within the NCS group. Furthermore, sulphur is a weak σ -donor, the M-S bond is stabilized, probably, by an additional π -back bonding²³⁹ from metal ion to sulphur atom. The characteristic M-S bond frequencies have been observed at the expected position¹²⁹ in the far i.r. region. The characteristic ν (M-Cl) and ν (M-P) stretching frequencies are also indicated at the appropriate positions¹³⁵. As the lone pair at phosphorus is free and does

not interact with the NCS bonding (vide supra), owing to its directional nature (sp^3 hybrid), coordination through phosphorus atom may not exhibit any observable effect on the stretching frequencies of the -NCS skeleton. It can therefore be emphasized that, like the unstable phospho-alkyne²³² the labile $(RP(NCS)_2)$, too, is stabilized via complex formation with metal and the $-P(NCS)_2$ moiety is retained in the complexes.

The ^{31}P n.m.r. spectra of the complexes recorded in d^6 DMSO showed a single resonance between +18 to +45 ppm region using 85% H_3PO_4 as external reference. The signal lies considerably up-field compared to that^{110,230,231} in the uncomplexed moiety but is in the range reported for transition metal phosphine complexes²⁴⁰. Thus chelation to metal ion is accompanied by a large increase in phosphorus shielding, probably due to additional overlap between the empty $P(3d \pi)$ and metal $(3d \pi)$ orbitals effecting the delocalization of the metal electrons. The observed broadening of the signal [excepting (XLIX), (L), (LVII) and (LVIII)] is due to the presence of paramagnetic species in the solution: may be arising as a result of dissociation or square-planar \rightleftharpoons tetrahedral or high spin \rightleftharpoons low spin equilibria.

The results of the reflectance spectra and magnetic susceptibility of the complexes have been summarized in

Table-XVIII. The observed magnetic moment value μ_{eff} of (XLV) and (XLVI) is in the range reported for high spin d^5 configuration of the metal ion. The reflectance spectra of (XLV) and (XLVI) are identical in nature containing weak bands in the visible (ligand field) region. The weak intensity of the bands is due to the forbidden nature of the originating transitions¹⁷⁵ arising from the 6S ground state to the quartet excited states derived from the 4G and 4D levels as indicated in Table-XVIII. In view of the present studies a tetrahedral geometry is proposed for (XLV) and (XLVI).

The μ_{eff} value of (XLVII) and (XLVIII) (Table-XVIII) indicates a high spin d^7 configuration of the cobalt ion in the complex. The position of the bands observed in the reflectance spectrum are characteristic of a tetrahedral environment around the cobalt ion.

The magnetic moment measurements for the complexes (XLIX) and (L) showed them to be diamagnetic in nature and the bands observed in the reflectance spectrum are characteristic of square-planar geometry¹⁷⁵ of nickel(II) ion. The ground state for the d^8 nickel complex is $^1A_{1g}$ and three peaks observed in the reflectance spectrum at 29,300, 23500 and 14,280 cm^{-1} for (XLIX) and 28,500, 23,800, 14,280 for (L) are assigned to the transition $^1B_{1g} \leftarrow ^1A_{1g}$, $^1A_{2g} \leftarrow ^1A_{1g}$ and $^3A_{2g} \leftarrow ^1A_{1g}$ respectively. The

diamagnetic nature of the compounds, further, confirms the square-planar geometry of the molecule.

The magnetic moment value of (LI) and (LII) is consistent with the d^9 configuration of the copper ion. A single broad band has been observed in the ligand field region of (LI) and (LII) [at $18,200\text{ cm}^{-1}$ (LI) and at $19,650\text{ cm}^{-1}$ (LII)] which can be assigned to the d-d transition of pseudo-tetrahedral environment around copper(II) ion. For regular tetrahedral copper (II) complexes the region $(10,000\text{--}20,000\text{ cm}^{-1})$ is reported¹⁷⁵ to be blank. The absence of a band in the $14,000\text{--}16,000\text{ cm}^{-1}$ region, however, rules out any possibility of square-planar geometry¹⁷⁵ for the complexes. These observations indicate that (LI) and (LII) is a genuine copper (II) complex which seems to constitute unusual behaviour of RP(NCS)_2 , compared with that known²⁴¹ for reactions of $(\text{C}_6\text{H}_5)_3\text{P}$ or substituted halophosphines with Cu(II) salts, which invariably result in redox process with generation of copper(I) species.

The μ_{eff} value of (LIII) and (LIV) is much lower from the calculated spin only value expected for high spin d^5 configuration of the metal ion. This is probably due to the antiferromagnetic interaction, a well known behaviour reported¹⁷⁴ for some of the iron complexes. The ligand field spectrum contained bands with weak intensities because the

excited states are of different spin multiplicity from the ground (6A_1) state. Out of the nine expected sextet-quartet transitions from 6A_1 to quartet excited states derived from 4G , 4D , 4P and 4F levels, the observed band positions with their assignments have been shown in Table-XVIII. The magnetic moment and observed bands in the reflectance spectrum of (LV) and (LVI) are indicative of a tetrahedral configuration around vanadium ion.

The compound (LVII) and (LVIII) were diamagnetic in nature. The expected diamagnetic nature of (LVII) and (LVIII) and absence of any ligand field bands are due to a d^{10} configuration of the metal ion. However, tetrahedral geometry may reasonably be proposed from the observed stoichiometry, non-electrolyte nature of the solutions and i.r. spectral informations.

TABLE-XVI

Important *i.r.* frequencies (cm^{-1}) and their assignments for $\text{RP}(\text{NCS})_2$ and the complexes.

Compounds	$\text{CH}_3/\text{C}_6\text{H}_5$ vibration	$\nu_{\text{asym. NCS}}$	$\nu_{\text{sym. NCS}}$	$\nu(\text{P-N})$	$\nu(\text{M-S})$	$\nu(\text{M-P})$	$\nu(\text{M-Cl})$
$\text{CH}_3\text{P}(\text{NCS})_2$	2960w, 2920w, 1390w, 1235s, 800m	2040s	960m	1155m	-	-	-
$\text{C}_6\text{H}_5\text{P}(\text{NCS})_2$	1590m, 1445vs, 1130s, 745s, 715m, 695vs	2020sb	970m	1160m	-	-	-
$[\text{Mn}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (XLV)	2955w, 2920w, 1390w, 1235s, 795m	2030s	955m, 920w	1150m,	290m	375w	300m
$[\text{Mn}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (XLVI)	1590m, 1440vs, 1120s, 750m, 725s, 690s	2020m	990m, 970w	1145m	275m	365m	300m
$[\text{Co}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (XLVII)	2950w, 2910w, 1395w, 1240, 810m	2060s	970m, 950w	1140m	280m	390w	295m
$[\text{Co}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (XLVIII)	1590m, 1450s, 1130m, 760m, 720s, 695s	2070s	980m, 965w	1150m	280m	350m	300m
$[\text{Ni}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (XLIX)	2950w, 2900w, 1390w, 1230s, 790m	2030s	970m, 950w	1140s	280m	350sh	320m
$[\text{Ni}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (L)	1590m, 1440vs, 1130s, 760m, 730vs, 695vs	2040sb	980m	1150m	275m	350sh	320m
$[\text{Cu}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (LI)	2970w, 2930w, 1390w, 1235s, 800m	2070s	960m, 930w	1160m	295m, 275w	345w	300m
$[\text{Cu}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}$ (LII)	1595m, 1430vs, 1130s, 740m, 730vs, 695vs	2060m	965m, 945w	1150m	290m, 270w	330sh	310m
$[\text{Fe}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}_2$ (LIII)	2960w, 2910w, 1380w, 1240s, 790m	2030m	980m	1140m	280m	320sh	300m
$[\text{Fe}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}_2$ (LIV)	1630m, 1420s, 1130s, 750m, 725s, 690s	2040m	970m	1145m	290m	325sh	310m
$[\text{V}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}_2$ (LV)	2950w, 2900w, 1390w, 1240s, 800s	2030m	950m	1140m	280m	350w	300m
$[\text{V}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]\text{Cl}_2$ (LVI)	1620m, 1420m, 1130s, 750m, 725m, 690s	2010m	960m, 940w	1150m	290m, 270w	360sh	305m
$[\text{Cu}(\text{CH}_3\text{P}(\text{NCS})_2)\text{Cl}]$ (LVII)	2960w, 2910w, 1300, 1250s, 810m	2070m	960mb	1155m	290m, 270w	330sh	300m
$[\text{Cu}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)\text{Cl}]$ (LVIII)	590m, 1440vs, 1135s, 750m, 730vs, 695vs	2080s	980m	1150m	290m, 265w	325sh	310m

vs = very strong, s = strong, m = medium, w = weak

TABLE-XVII

Physical data of the $RP(NCS)_2$ complexes.

Complexes	M.pt (°C)	Colour	Found (Calculated)%					$\Lambda_M(\text{Ohm}^{-1}\text{cm}^2\text{Mol}^{-1})$
			C	H	N	Cl	M	
$[\text{Mn}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (XLV)	150	light yellow	12.62 (12.51)	1.02 (1.04)	9.52 (9.73)	23.98 (24.63)	19.91 (19.09)	67
$[\text{Mn}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (XLVI)	175	-do-	27.44 (27.44)	1.40 (1.40)	8.3 (8.0)	20.84 (20.27)	16.20 (15.68)	71
$[\text{Co}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (XLVII)	260	greenish yellow	12.41 (12.34)	1.06 (1.03)	9.35 (9.60)	24.95 (24.30)	20.85 (20.20)	56
$[\text{Co}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (XLVIII)	310	-do-	27.13 (27.11)	1.43 (1.40)	7.6 (7.6)	20.2 (20.0)	16.4 (16.6)	54
$[\text{Ni}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (XLIX)	235	yellow	12.27 (12.35)	1.02 (1.03)	9.58 (9.60)	24.15 (24.32)	20.36 (20.13)	60
$[\text{Ni}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (L)	280	-do-	21.16 (21.14)	1.40 (1.42)	7.90 (7.90)	20.12 (20.00)	16.18 (16.00)	67
$[\text{Cu}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (LI)	147	chocolate	12.18 (12.14)	1.06 (1.01)	9.42 (9.44)	23.75 (23.92)	21.52 (21.43)	53
$[\text{Cu}(\text{C}_6\text{H}_5\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}]$ (LII)	280	-do-	27.05 (27.00)	1.42 (1.40)	7.84 (7.82)	19.76 (19.78)	17.92 (17.7)	55
$[\text{Fe}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}_2]$ (LIII)	140	orange	11.07 (11.10)	0.91 (0.93)	8.58 (8.64)	32.78 (32.81)	17.12 (17.23)	118
$[\text{Fe}(\text{CH}_3\text{H}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}_2]$ (LIV)	165	-do-	24.80 (24.85)	1.34 (1.30)	7.0 (7.20)	27.50 (27.54)	14.40 (14.44)	121
$[\text{V}(\text{C}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}_2]$ (LV)	160	greenish yellow	11.31 (11.28)	1.02 (0.94)	8.81 (8.77)	33.81 (33.31)	16.22 (15.95)	116
$[\text{V}(\text{CH}_3\text{H}_3\text{P}(\text{NCS})_2)_2\text{Cl}_2\text{Cl}_2]$ (LVI)	195	-do-	25.15 (25.17)	1.30 (1.32)	7.35 (7.35)	27.93 (27.90)	13.51 (13.34)	115
$[\text{Cu}(\text{CH}_3\text{P}(\text{NCS})_2)_2\text{Cl}]$ (LVII)	202	off-white	13.81 (13.79)	1.16 (1.15)	10.72 (10.73)	13.67 (13.58)	24.95 (24.35)	20
$[\text{Cu}(\text{CH}_3\text{H}_3\text{P}(\text{NCS})_2)_2\text{Cl}]$ (LVIII)	230	-do-	29.74 (29.72)	1.49 (1.50)	8.40 (8.60)	11.21 (10.98)	20.05 (19.65)	15

TABLE-XVIII

 μ_{eff} (B.M.)* and Reflectance spectra (cm^{-1}) with probable assignments.

Complexes	μ_{eff}	Band positions	Assignment
[Mn{RP(NCS) ₂ }Cl]Cl	5.9	(<u>XLV</u>), (<u>XLVI</u>)	
		44, 380, 38, 500, 32, 250	c. t.
		(43, 480, 38, 460, 31, 350)	
		27, 560 (27, 800)	${}^4\text{E}(\text{D}) < \text{-----} {}^6\text{A}_1$
		26, 110 (26, 300)	${}^4\text{T}_2(\text{D}) < \text{-----}$
		24, 720 (24, 640)	${}^4\text{A}_1, {}^4\text{E}(\text{G}) < \text{---}$
		19, 890 (20, 200)	${}^4\text{T}_2(\text{G}) < \text{-----}$
[Co{RP(NCS) ₂ }Cl]Cl	4.3 (4.32)	43, 100, 31, 920, 30, 300	c. t.
		(42, 500, 31, 760, 30, 300)	
		16, 680 (16, 950)	${}^4\text{T}_1(\text{P}) < \text{-----} {}^4\text{A}_2$
[Ni{RP(NCS) ₂ }Cl]Cl	diamag. -do-	43, 500, 39, 260, 30, 920	c. t.
		(43, 480, 39, 250, 31, 250)	
		29, 300 (28, 500)	${}^1\text{B}_{1g} < \text{-----} {}^1\text{A}_{1g}$
		23, 500 (23, 800)	${}^1\text{A}_{2g} < \text{-----}$
		14, 280 (14, 500)	${}^3\text{A}_{2g} < \text{-----}$
[Cu{RP(NCS) ₂ }Cl]Cl	1.81 (1.83)	43, 850, 38, 510, 32, 000	c. t.
		(43, 480, 38, 720, 31, 750, 18, 200 (19, 650)	

Table-XVIII Contd...

Complexes	μ_{eff}	Band positions	Assignment
[Fe{RP(NCS) ₂ }Cl]Cl ₂ (<u>LIII</u>), (<u>LIV</u>)	1.83	44,250, 39,350, 33,640	c.t.
	(4.55)	(43,480, 40,570, 33,330)	
		28,270 (28,020)	⁴ E(D) <----- ⁶ A ₁
		27,130 (27,030)	⁴ T ₂ (D) <-----
		25,640 (25,640)	⁴ A ₁ , E(G) <---
		22,250 (22,200)	⁴ T ₂ (G) <-----
[V{RP(NCS) ₂ }Cl]Cl ₂ (<u>LV</u>), (<u>LVI</u>)	4.2	42,310, 38,510, 38,435	c.t.
	(4.22)	(41,660, 37,740, 38,900)	
		14,480 (14,500)	³ T ₁ <----- ³ A ₂
		11,240 (11,230)	³ T ₂ <-----

* B.M. = 0.927×10^{-23} J.T.⁻¹, c.t. = charge transfer bands, data for complexes with R = C₆H₅ in parentheses.

1. Coryell and Pauling, J. Biol. Chem., 132, 769 (1940).
2. G.M. Badger, "Aromatic Character and Aromaticity" Cambridge University Press, London, pp.1-37 (1969).
3. S. Martinez - Carrera, Acta Crystallogr., 20, 783 (1966).
4. G. Berthier, L. Praud and J. Serre, "Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry", Edited by E.D. Bergman and B. Pullman, Isr. Acad. Sc., Jerusalem, 40 (1970).
5. Y. Chiang and E.B. Whipple, J. Am. Chem. Soc., 85, 2763 (1963).
6. H.J. Chen, L.E. Hakka, R.L. Hinman, A.J. Kresge and E.B. Whipple, J. Am. Chem. Soc., 93, 5102 (1971).
7. G. Yagil, Tetrahedron, 23, 2855 (1967).
8. H. Walba and R.W. Isensee, J. Org. Chem., 21, 702 (1956).
9. P. George, G.I.H. Hanania, D.H. Irvine and I. Abu-Issa, J. Chem. Soc., 5689 (1964).
10. J.D. Vaughan, Z. Mughrabi and E.C. Wu, J. Org. Chem., 35, 1141 (1970).
11. G.R. Lenz and A.E. Martell, Biochemistry, 3, 750 (1964).
12. J.E. Letter Jr. and R.B. Jordan, Inorg. Chem., 10, 2692 (1971).
13. A.D. Mighell and A. Santoro, Acta Crystallogr., B27, 2089 (1971).
14. L.G. Marzilli and P.A. Marzilli, Inorg. Chem., 11, 457 (1972).
15. H.C. Freeman and J.T. Szymanski, Acta Crystallogr., 22, 406 (1967).
16. Auvermann, Arch. Expt. Pathol. Pharmacol, 81, 155 (1918).
17. Leitler, J. Biol. Chem. 64, 125 (1925).
18. Leoper, Mougeot and Aubertot, Compt. Rend. Soc. Biol., 116, 33 (1954).

19. R.M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", 2nd Edit, Wiley Eastern Limited, New Delhi, Chpater VII, 311 (1967).
20. J.A. Joule, G.F. Smith, "Heterocyclic Chemistry", Published by Van Nostrand Reinhold Comapny Ltd., Molly Millers Lane, Wokingham, Berkshire, England, IInd Eidt, Chpater XXVI, 303 (1978).
21. Ger. Pat., 703, 899 (Feb. 13, 1941); U.S. Pat., 2, 399, 601 (Aug.30, 1946).
22. Supniewski, Compt. Rend. Soc. Biol., 98, 1229 (1928).
23. U.S. Pat., 2, 404, 300 (Jul. 16, 1946).
24. McDonagh, Brit. J. Dermatol. Syphilis, 37, 30 (1925).
25. Dale and Laidlow, J. Physiol., 41, 318 (1910).
26. Best and McHenery, Physiol. Revs., 11, 371 (1931).
27. Schenk, Arch. Exptl. Pathol. Pharmacol., 92, 34 (1922).
28. E.S. Schipper and A.R. Day, "Heterocyclic Compounds", Edited by R.C. Elderfield, John Wiley and Sons, New York, Chapman and Hall Ltd., London, 5, 225 (1957).
29. F.A. Robinson, "The Vitamin B-Complex", Chapman and Hall Ltd., London, 533 (1951).
30. C.A. Matuszak and A.J. Matuszak, J. Chem. Educ. 53, 280 (1976).
31. T.L. Blundell, G.G. Dodson, D.C. Hodgkin and M. Vijayan, Recent. Adv. Horm. Res., 27, 19 (1971).
32. A.I. Busevand, Min-Tiao Huang, Z. Analit. Khim., 17, 1091 (1962).
33. H.J. Zimmer Fr., 14,00, 174 (May 21, 1965); Ger. Appl., (Jul. 17, 1963).
34. E. Schraufstatter, Z. Naturforsch., 5B, 190 (1950).
35. J. Reedijk and J.K. DeRidder, Inorg. Nucl. Chem. Lett., 12, 585 (1976); H. Tamura and H. Imai, J. Am. Chem. Soc., 109, 6870 (1987).
36. P.P. Parellada, G.G. Gasulla and P.P. Muset, Pharmacol., 10, 161 (1973).

37. K. Hofmann, "Imidazole and its derivatives", Interscience, New York, Part I, 15 (1953).
38. D.M.L. Goodgame, M. Goodgame, P.J. Hayward and G.W. Rayner Canham, *Inorg. Chem.*, **7**, 2447 (1968).
39. C.E. Taylor and A.E. Underhill, *J. Chem. Soc. A*, 368 (1969).
40. S.V. Deshpande and T.S. Srivastava, *Polyhedron* **2**, 761 (1983).
41. T.N. Hazarika and T. Bora *Polyhedron*, **1**, 121 (1984).
42. J. Reedijk, *Recl. Trav. Chim*, **88**, 1451 (1969) and references cited therein.
43. D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.*, **97**, 1403 (1975).
44. B.S. Tovrog and R.S. Drago, *J. Am. Chem. Soc.*, **96**, 2743 (1974).
45. A. Albert, "Physical Methods in Heterocyclic Chemistry", Edited by I.R. Katritzky, Academic Press, New York, **1** (1963).
46. A.D. Gornovskii, O.A. Osipov, V.T. Panyushin and A.F. Pozharskii, *Zh. Obsh. Khim*, **36**, 1063 (1963).
47. V.T. Panyushin, A.D. Gornovskii, O.A. Osipov, A.L. Siyavin and A.F. Pozharskii, *Zh. Obsh. Khim.*, **37**, 312 (1967).
48. B.K.S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1966).
49. W.J. Eilbeck, F. Holms and A.E. Underhill, *J. Chem. Soc.*, 757 (1967).
50. C. Sandmark and C.I. Bränden, *Acta. Chem. Scand.*, **21**, 993 (1967).
51. J.C. Wang and J.E. Bauman, *Inorg. Chem.*, **4**, 1961 (1965).
52. F. Seel and V. Sperber, *Angew. Chem. Int. Ed. Engl.*, **7**, 70 (1968).
53. J.E. Bauman Jr. and J.C. Wang. *Inorg. Chem.*, **3**, 368 (1964).
54. G.P. Brown and S. Aftergut, *J. Polym. Sci., Part A*, **2**, 1839 (1964).

55. J.A. Jarvis and A.F. Wells, *Acta Crystallogr.*, **13**, 1027 (1960); Cf. Appendix III in H.C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).
56. M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem*, **4**, 626 (1965); *Bull. Chem. Soc. Jap.*, **39**, 1352 (1966).
57. C. Sigwart, P. Kroneck and P. Hemmerich, *Helv. Chim. Acta.*, **53**, 177 (1970).
58. F. Akhtar, F. Haq and A.C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1353 (1972).
59. C.B. Acland and H.C. Freeman, *Chem. Commun.*, 1016 (1971).
60. C.J. Antti and B.K.S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1966).
61. B.K.S. Lundberg, *Acta. Chem. Scand.*, **26**, 3977 (1972).
62. G. Ivarsson, B.K.S. Lundberg and N. Ingri, *Acta. Chem. Scand.*, **26**, 3005 (1972).
63. H.C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).
64. D.J. O'Sullivan and F.J. Lalor, *J. Organometal. Chem.*, **25**, C80 (1970).
65. F. Seel and V. Sperber, *J. Organometal. Chem.*, **14**, 405 (1968).
66. K.K. Joshi, P.L. Pauson, A.R. Qazi and W.H. Stubbs, *J. Organometal. Chem.*, **1**, 471 (1964).
67. R.B. King and M.B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964).
68. R.J. Sundberg, R.E. Shepherd, H. Taube, *J. Am. Chem. Soc.*, **94**, 6558 (1972).
69. R.J. Sundberg, R.F. Bryan, I.F. Taylor Jr., H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).
70. M.J. Clarke and H. Taube, *J. Am. Chem. Soc.*, **97**, 1397 (1975).
71. M.F. Tweedle and H. Taube, *Inorg. Chem.*, **21**, 3361 (1982).
72. K. Ofele and C.G. Kreiter, *Chem. Ber.*, **105**, 529 (1972).

73. K. Ofele, *J. Organometal. Chem.*, **12**, 42 (1968).
74. H.J. Schönhere and H.W. Wanzlick, *Chem. Ber.* **103**, 1037 (1970).
75. G. Hüttner and W. Gartzke, *Chem. Ber.*, **105**, 2714 (1972).
76. P. Luger and G. Ruban, *Acta Crystallogr.*, **B27**, 2276 (1971).
77. M. Inoue and M. Kubo, *Coord. Chem. Rev.*, **21**, 1 (1976).
78. S.E. Groh, *Isr. J. Chem.*, **15**, 277 (1976-1977).
79. V. Casellato, P.A. Vigato, D.E. Fenton, M. Vidali, *Chem. Soc. Rev.*, 199 (1979).
80. J.A. Ibers, R.H. Holm, *Science (Washington, D.C.)*, **209**, 223 (1980).
81. O. Kahn, J. Claude, H. Coudanne, *Nouv. J. Chim*, 167 (1980) and references cited therein.
82. J.S. Richardson, K.A. Thomas, B.H. Rubin, D.C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1349 (1975).
83. G. Palmer, G.T. Babcock, L.E. Vickery, *Proc. natl. Acad. Sci. U.S.A.*, **73**, 2206 (1976).
84. R.J. Sundberg, R.B. Martin, *Chem. Rev*, **74**, 471 (1974).
85. M.E. McAdam, E.M. Fielden, F. Lavalley, L. Calabrese, D. Cocco, G. Rotilio, *J. Biochem*, **167**, 271 (1977) and references cited therein.
86. B.K.S. Lundberg, *Acta. Chem Scand.*, **26**, 3902 (1972).
87. G. Kolks, C.R. Frihart, H.N. Rabinowitz and S.J. Lippard, *J. Am Chem. Soc.*, **98**, 5720 (1976).
88. G. Kolks, S.J. Lippard, *J. Am. Chem. Soc.*, **99**, 5804 (1977).
89. S.A.A. Zaidi, T.A. Khan, Z.A. Siddiqi, *Synth. React. Inorg. Met-Org. Chem.*, **14**, 717 (1984).
90. S.A.A. Zaidi, T.A. Khan, S.R.A. Zaidi, Z.A. Siddiqi, *Polyhedron*, **4**, 1163 (1985).
91. S.A.A. Zaidi, T.A. Khan, S.A. Shaheer, S.R.A. Zaidi, Z.A. Siddiqi, *Bull. Soc. Chim. Fr.*, **4**, 536 (1986).

92. S.A.A. Zaidi, T.A. Khan, Z.A. Siddiqi, *Bull. Soc. Chim. Fr.*, 5-6, 149 (1984).
93. S.A.A. Zaidi, T.A. Khan, S.A. Shaheer and S.R.A. Zaidi, *Acta. Chim. Hung.* 125, 229 (1988).
94. S.A.A. Zaidi, T.A. Khan and S.R.A. Zaidi, *Ind. J. Chem.*, 29A, 916 (1990).
95. P.C.H. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912 (1960).
96. M. M. Chamberlain and J.C. Bailor Jr., *J. Am. Chem. Soc.*, 81, 6412 (1959).
97. Penney and Sutherland, *Proc. Roy. Soc., A*, 156, 654 (1936).
98. Chatt, Duncanson, Hart and Owstan, *Nature*, 178, 997 (1956); *ibid*, 181, 43 (1958).
99. J.F. Villa and H.B. Powell, *Synth. React. Inorg. Met. - Org. Chem.*, 6, 59 (1976).
100. Monsanto Chem. Co. British Patent, 795051; *Chem. Abstr.*, 52, 18962c (1958).
101. E. Plohte, J. Grundues and P. Klæboe, *Acta. Chem. Scand.*, 19, 1897 (1965).
102. B. B. Wayland and R.H. Gold, *Inorg. Chem.*, 5, 154 (1966).
103. J.F. Villa and H.B. Powell, *Inorg. Chim. Acta.*, 32, 199 (1979).
104. M.C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).
105. T. Wintink, *J. Chem. Phys.*, 29, 189 (1958); M.S. Ham and J.B. Willis, *Spectrochim. Acta*, 16, 279 (1960).
106. G.I. Derkatsch, *Angew. Chem.*, 8, 424 (1969) and references cited therein.
107. A.E. Dixon, *J. Chem. Soc.*, 79, 541 (1901); J.E. Reynolds, *J. Chem. Soc.*, 89, 397 (1906); P. Miquel, *Ann. Chim. Phys.*, 11, 341 (1877).
108. D.T. Elmore, J.R. Ogle, *J. Chem. Soc.*, 2286 (1959).
109. H.H. Anderson, "Silicon Sulphur and Phosphates", *Colloquium of the Section for Inorganic Chemistry of the*

International Union of Pure and Applied Chemistry,
Münster, pp.37 and 235 (1954).

110. D.B. Sowerby, J. Inorg. Nucl. Chem., 22, 205 (1961).
111. G. Tesi, R.J.A. Otta, F.G. Sherif and L.F. Audrieth, J. Am. Chem. Soc., 82, 528 (1960).
112. D.T. Elmore, J.R. Ogle, W. Fletcher and P.A. Toseland, J. Chem. Soc., 4458 (1956).
113. R. Riemachneider and G. Orlick, Monatsh. Chem., 84, 313 (1953); A.P. Terentyev and A.J. Gershenovich, J. Gen. Chem., U.S.S.R., 23, 209 (1953).
114. A.E. Dixon and J. Taylor, J. Chem. Soc., 93, 2148 (1908).
115. L. Maier, Helv. Chim. Acta., 46, 2667 (1963).
116. M. Fild, Z. Naturforsch., 23B, 604 (1968).
117. K.B. Dillon, R.N. Reeve and T.C. Waddington, J. Chem. Soc. Dalton Trans., 1410 (1977).
118. Wright and Hunter, J. Am. Chem. Soc., 69, 803 (1947).
119. Clark, Gordon, Young and Hunter, J. Am. Chem. Soc., 73, 3798 (1951).
120. Smith, J. Chem. Phys., 21, 1997 (1953).
121. U. Wannagat, "Advances in Inorganic Chemistry and Radiochemistry Series", 6, 232 (1964).
122. E.A.V. Ebsworth and J.J. Turner, J. Phys. Chem, 67, 805 (1963).; D. Kummar and J.D. Baldschwieler, J. Phys. Chem., 67, 98 (1963).
123. R.H. Carlson and T.L. Brown, Inorganic Chemistry, 5, 268 (1966).
124. J. Reedijk, J. Inorg. Nucl. Chem., 33, 179 (1970).
125. "Organic Phosphorus Compounds", Edited by G.M. Kosolpoff and L. Maier, Published by Wiley Inter Science, 1, 97 (1972).
126. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", Chapman and Hall London, IIIRD Edit., 1, Chapter-XX, 375 (1975).

127. L. Maier, "Progress in Inorganic Chemistry", Interscience Publishers, 5, 140 (1963).
128. J. Lewis, R.S. Nyholm and P.W. Smith, J. Chem. Soc. 4590 (1960) and references cited therein.
129. A. Sabatini and I. Bertini, Inorg. Chem., 4, 959 (1965).
130. G.I. Childow and H.W. Thomson, Spectrochim Acta., 212 (1958); C.V. Stephenson, W.S. Coburn Jr. and W.S. Wilcox, Spectrochim Acta., 17, 940 (1961).
131. K. Nakamoto, "Infra-red Spectra of Inorganic and Coordination Compounds", John Wiley and Sons Inc., New York, 146 (1963).
132. B. Cornilsen and K. Nakamoto, J. Inorg. Nucl. Chem., 36, 2467 (1974).
133. "Modern Coordination Chemistry: Principles and Methods", Edited by J. Lewis and R.G. Wilkins, Interscience Publishers Inc., New York, 365 (1960) and references cited therein.
134. E. Niecke, D. Gudat, E. Symalla, Angew. Chem. Int. Ed. Engl., 25, 834 (1986).
135. R.J.H. Clark and C.S. Williams, Inorg. Chem., 4, 350 (1965).
136. R.J.H. Clark and C.S. Williams, Spectrochim Acta., 23A, 1055 (1967).
137. K.C. Malhotra and Balkrishan, J. Inorg. Nucl. Chem., 39, 387 (1977).
138. K. Nakamoto, "Infra-red and Raman Spectra of Inorganic and Coordination Compounds", IVth Edit, John Wiley and Sons, New York, pp.338, 341 (1986).
139. G. Mavel, Compt. Rend., 248, 3699 (1959).
140. "Modern Coordination Chemistry: Principles and Methods", Edited by J. Lewis and R.G. Wilkins, Interscience Publishers Inc. New York, Chapter IV, 287 (1960).
141. H. Hartmann and H.L. Schläfer, Z. Naturforsch., 6A, 754, 766 (1951).
142. C.J. Ballhausen, Recl. Trav. Chim., 75, 655 (1956); G. Maki, J. Chem. Phys., 29, 1129 (1958).

143. H. Hartmann and H. Fisher - Wasels, Z. Physik. Chem. (Frankfurt), 4, 297 (1955).
144. C.J. Ballhausen and A.D Liehr, J. Am. Chem. Soc., 81, 538 (1959).
145. C.K. Jørgensen, Acta. Chem. Scand., 10, 518 (1956).
146. H. Hartmann and C. Buschbeck, Z. Physik. Chem. (Frankfurt), 11, 120 (1957).
147. W.J. Geary, Coord. Chem. Rev., 7, 81 (1971).
148. D. Sobale. and N. Bobrov, "Physical Chemistry of Polymers", Mir Publishers, Moscow, Chapter-XV and XVI (1978).
149. F.G. Mann and B.C. Saunders, "Practical Organic Chemistry", Longman, London, 435 (1961).
150. I. M. Kolthoff, E.B. Sandell, E.J. Meehan and S. Bruckenstein, "Qualitative Chemical Analysis", McMillan Ltd., London, 580 (1969).
151. C.N. Reilley, R.W. Schmid, F.A. Sadak, J. Chem. Educ., 36, 619 (1959); A.I. Vogel, "A Text Book of Inorganic Analysis", IIIrd Edit., Longman, London, (1964).
152. "Vogel's Text Book of Quantitative Inorganic Analysis", Revised by J. Bassett, R.C. Denney, G.H. Jeffery, J. mendham, IVth Edit., ELBS, Longman, London, Chapter-XI, 484 (1978).
153. J. Anhaus, Z.A. Siddiqui, J. Schimkoviak and H.W. Roesky, Z. Naturforsch., 39B, 1722 (1984).
154. L. Birkofer P. Richter and A. Ritter, Chem. Ber., 99, 2804 (1960) *ibid*, 99, 2810 (1960).
155. H.A. Staab, Chem. Ber., 89, 1927 (1956).
156. "Vogel's Textbook of Practical Organic Chemistry", IVth Edit, Chapter-II (1978).
157. D.A. Armiteage, H.J. Clark, A.W. Sindon, J.N. wingfield, E.W. Abel and E.J. Louis (Section A), "Inorganic Syntheses", McGraw Hill Book Co., New York, 15, 207 (1974).
158. G. Brauer, "Handbook of Preparative Inorganic Chemistry", Academic Press, New York, London, 2, 1515, 1008 (1965).

159. H.A. Tayim, A. Bouldoukian and F. Awad, J. Inorg. Nucl. Chem., 32, 3799 (1970).
160. G. Costa, G. Pellizer and F. Rubessa, J. Inorg. Nucl. Chem., 26, 961 (1964).
161. T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28, 945 (1966).
162. R. Bonnett, D.C. Bradley and K.J. Fisher, Chem. Commun., 1967 (1968); *ibid*, J. Chem. Soc., A, 1622 (1971).
163. D.C. Bradley, Chem. Brit., 11, 393 (1975).
164. H. Bürger and U. Wannagat, Monatsh. Chem., 94, 1007 (1963); *ibid*, 95, 1099 (1964); D.C. Bradley and K.J. Fisher, J. Am. Chem. Soc., 93, 2058 (1971).
165. D.C. Bradley, M.B. Hursthouse, R.J. Samllwood and A.J. Welch, Chem. Commun., 872 (1972).
166. G. Booth "Advances in Inorganic and Radiochemistry", Edited by H.J. Emeleus and A.G. Sharpe, 6, 1 (1964) and references cited therein.
167. H. Bürger, W. Sawodny and U. Wannagat, J. organometal. Chem., 3, 113 (1965).
168. A.D. Liehr, J. Chem. Educ., 39, 135 (1962).
169. J.T. Hougen, G.E. Leroi and T.C. James, J. Chem. Phys., 34, 1670 (1961); C.W. DeKock and D.M. Gruen, *ibid*, 44, 4387 (1966).
170. F.A. Cotton, D.M.L. Goodgame, M. Goodgame and A. Sacco, J. Am. Chem. Soc., 83, 4157 (1961).
171. C.J. Ballhausen, "Introduction to Ligand Field Thoery", McGraw Hill' Book Co. Inc. Corp. Ltd., New York, Chapter-X (1962).
172. B.N. Figgis and J. Lewis, "Modern Coodination Chemistry", Edited by L. Lewis and R.G. Wilkins, Interscience, New York, Chapter-VI (1960).
173. I.M. Procter, B.J. Hathaway and P. Nichollis, J. Chem. Soc., A, 1678 (1968); A. Longo and T. Buch., Inorg. Chem., 6, 556 (1967).
174. B.N. Figgis and J. Lewis, "Progress in Inorganic Chemistry", Edited by F.A. Cotton, Interscience Publishers, New York, 6, 37 (1964).

175. A.B.P. Lever, "Inorganic Electronic Spectroscopy" IInd Edit, Elsevier, Amsterdam (1984).
176. B. Morosin and E.C. Lingafelter, *Acta Crystallogr.*, **13**, 807 (1960).
177. N.S. Gill and R.S. Nyholm, *J. Chem. Soc.*, 3997 (1959); D.M.L. Goodgame and F.A. Cotton, *J. Chem. Soc.*, 2998 (1961).
178. K. Nakamoto, "infra-red and Raman Spectra of Inorganic and Coordination compounds", John Wiley and Sons, New York, IVth Edit., 192 (1986).
179. Z.A. Siddiqi, M. Shakir, T.A. Khan and S.A.A. Zaidi, *Synth. React. Inorg. Met. Org. Chem.*, **13**, 397 (1983).
180. G. Brewer and R. Wang, *Chem. Commun.*, **7**, 583 (1990).
181. H.S. Sangri, G.S. Sodhi, *Ind. J. Chem.*, **29**, 922, (1990); B.N. Figgis, "Introduction to ligand Fields", Wiley Eastern, New Delhi (1976).
182. B.N. Figgis and J. Lewis, "Modern Coordination Chemistry: Principles and Methods" Edited by J. Lewis and R.G. Wilkins, Interscience Publishers Inc., New York, Chapter-VI, 435 (1960).
183. K.W. Fung and K.E. Johnson, *Inorg. Chem.*, **10**, 1347 (1971).
184. A.M. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).
185. G.B. Deacon and J.H.S. Green, *Chem. Indust.*, 1031 (1965) and references cited therein.
186. D. Fenske, J. Hachgenei, J. Ohmer, *Angew. Chem.*, **97**, 684 (1985); *ibid*, **97**, 993 (1985); *ibid*, *Angew. Chem. Int. Ed. Engl.*, **24**, 706 (1985); *ibid*, **24**, 993 (1985).
187. L. M. Venanzi, *J. Chem. Soc.*, **I**, 719 (1958).
188. R.A. Michelin, G. Facchin and P. Vguagliati, *Inorg. Chem.*, **23**, 961 (1984).
189. G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).
190. B.T. Kilbourn, *Proc. Chem. Soc.*, 207 (1963).
191. R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

192. R.H. Holm, J. Am. Chem. Soc., **82**, 5632 (1960).
193. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Vth Edit., John Wiley and Sons Publication, Chapter-IX, 921 (1988).
194. M. Nonoyame, Trans. Met. Chem. (Weinheim. Ger.), **12**, 1 (1987).
195. Y. Fuchita, M. Nakashima, K. Hiraki, M. Kawatani and K. Ohnuma, J. Chem. Soc. Dalton Trans., 785 (1988).
196. F. Bonati and H.C. Clark, Can. J. Chem., **56**, 2513 (1978).
197. M.T. Pinillos, C. Tejel, L.A. Oro, M.C. Apreda, C. Foces-Foces and F.H. Cano, J. Chem. Soc. Dalton Trans., 1133 (1989).
198. K. Nakamaoto, "Infra-red and Raman Spectra of Inorganic and Coordination Compounds", IVth Edit., John Wiley and Sons, New York, 199 (1986).
199. K. Shebatak and K. Nakamoto, J. Am. Chem. Soc., **92**, 3332 (1970).
200. J. Chatt, G.A. Gamlen and L.E. Orgel, J. Chem. Soc., 486 (1958) and references cited therein.
201. McGarvey, J. Phys. Chem., **60**, 71 (1956).
202. M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, "Metal and Metalloid Amides: Synthesis Structures and Physical and Chemical Properties", Harwood-Wiley, Chichester (1980).
203. H. Breederveld, Recl. Trav. Chim., **81**, 276 (1962).
204. P.G. Harrison and J.J. Zuckerman, Chem. Commun., 321 (1969).
205. J.G.A. Luijten and G.J.M. Vander Kerk, Recl. Trav. Chim Pays-Bas, **81**, 202 (1962); J.G.A. Luijten, M.J. Janssen and G.J.M. Vander Kerk, ibid, **82**, 1181 (1963).
206. J.G.A. Luijten and G.J.M. Vander Kerk, Recl. Trav. Chim. Pays-Bas, **83**, 295 (1964).
207. L. Birkofer and P. Wegner. Chem. Ber., **99**, 2512 (1966).
208. K. Sisido, K. Nabika, T. Isada and S. Kozima. J. Organometal. Chem., **33**, 337 (1971).

209. S. Kozima, T. Itano, N. Mihara, K. Sisido, T. Isada, J. Organomet. Chem., **44**, 117 (1972) and references cited therein.
210. P.G. Harrison and J.J. Zückerman, Inorg. Nucl. Chem. Lett., **5**, 545 (1969).
211. T. Fjelberg, H. Hope, M.F. Lappert, P.P. Power, A.J. Thorne, Chem. Commun., 639 (1983).
212. M.F. Lappert, P.P. Power, M.J. Slade, K. Hedberg, V. Schomaker, Chem. Commun., 369 (1979).
213. B. Centikaya, I. Gümrükcü, M.F. Lappert, J.L. Atwood, R.D. Rogers, M.J. Zaworotko, J. Am. Chem. Soc. **102**, 2088 (1980).
214. M. Olmstead and P.P. Power, Inorg. Chem., **23**, 413 (1984).
215. "Handbook of Preparative Inorganic Chemistry", Edited by G. Brauer, Academic Press, New York, London, 728 (1963).
216. W.L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall Inc., Englewood Cliffs, N.J., 480 (1970).
217. G.E. Coats and D. Ridley, J. Chem. Soc., 166 (1964).
218. R.C. Evans, F.G. Mann, H.S. Pieser and D. Purdie, J. Chem. Soc., 1209 (1940).
219. L.J. Bellamy, "Infrared Spectra of Complex Molecules", Chapman and Hall, London, IIrd Edit., Chapter-II, 13 (1975).
220. H. Bürger and W. Sawodny J. Inorg. Nucl. Chem. Lett., **2**, 209 (1966); *ibid*, Spectrochim. Acta., **23A**, 2841 (1976).
221. A.H. Cowley, D.M. Giolando, R.A. Jones, C.M. Munn and J.M. Power. Polyhedron, **7**, 1317 (1988).
222. P. Foley and M. Zeldin, Inorg. Chem., **14**, 2264 (1975).
223. J.D. Donaldson and D.G. Nicholson, J. Chem., Soc., A, 145 (1970).
224. H.E. Mabrouk and D.G. Tuck, J. Chem. Soc., Dalton Trans., 2539 (1988).
225. R.H. Crabtree, "The Organometallic Chemistry of the Transition Metals", Wiley, New York, 219 (1988).

- 226. J.C. Bailor Jr., H.J. Emeleus, R.H. Nyholm and A.F. Trotman - Dickenson, "Comprehensive Inorganic Chemistry", Pergamon Press, New York, 2, 58 (1973).
- 227. K. Ramaiah and D.F. Martin, Chem. Comm., 7, 130 (1965).
- 228. B.C. Cornilsen and K. Nakamoto, J. Inorg. Nucl. Chem., 36, 2467 (1974).
- 229. E. Kühle, B. Anders and G. Zumach, Angew. Chem. Int. Edit. Engl., 8, 421 (1969).
- 230. R. Ali and K.B. Dillon, Polyhedron, 5, 1197 (1986) and references cited therein.
- 231. K. Oba, F. Watari, K. Aida, Spectrochim. Acta., 23A, 1545 (1967).
- 232. J.C.T.R. Burkett Sr., L.P.B. Hitchcock, H.W. Kroto, J.F. Nixon, Soc. Chem. Commun., 1141 (1981).
- 233. O. Glemser, "Handbook of Preparative Inorganic Chemistry", Edited by G. Brauer, I, 671 (1963).
- 234. L.M. Jones and R.M. Badger, J. Chem. Phys., 18, 1311 (1950); C. Raid, *ibid.*, 18, 1512 (1950); B.P. Dailey *ibid.*, 18, 1437 (1950).
- 235. E. Duff, S. Tripett, P.J. Whittle, J. Chem. Soc. Perkin I, 972 (1973).
- 236. J.O. Edwards, "Inorganic Reaction Mechanism, W. Benjamin, New York, 57 (1965).
- 237. H.D. Smith Jr., M.A. Robinson, S. Papetti, Inorg. Chem., 6, 101 (1967).
- 238. R.G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).
- 239. A. Turco and C. Pecile, Nature, 66, 191 (1961).
- 240. R.H. Crabtree, "The Organometallic Chemistry of the Transition Metals", John Wiley, New York, 219 (1988).
- 241. C.A. McAuliff, W. Levasone, "Phosphine, Arsine and Stibine Complexes of the Transition Elements", I (1979).

Reactions of *N*-trimethylsilyl-imidazole and -2-methylimidazole with anhydrous CoCl_2 and $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$; synthesis and physicochemical studies on two-coordinate cobalt(II) complexes

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Summary

Reactions of *N*-trimethylsilylimidazole and *N*-trimethylsilyl-2-methylimidazole with CoCl_2 yield chloro(imidazolato)cobalt(II) (1), or chloro(2-methylimidazolato)cobalt(II) (2). However, the corresponding reactions of $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ cause total removal of Ph_3P along with the substitution of both the chlorine atoms yielding bis(imidazolato)cobalt(II) (3), or bis(2-methylimidazolato)cobalt(II) (4), in the form of light blue microcrystalline solids. The complexes have been characterized by elemental analysis, molecular weight, and magnetic susceptibility measurements, and i.r., reflectance and electronic spectra. The results are consistent with formulations as rare examples of two-coordinate cobalt(II) derivatives.

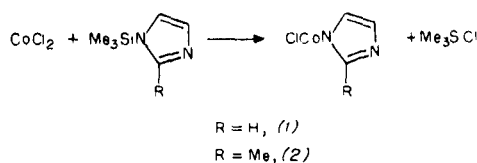
Introduction

Transition metal complexes of imidazole have been the subject of considerable investigations during the last two decades because they are models for histidyl residues of proteins or of bovine erythrocyte superoxide dismutase. Attempts by previous workers⁽¹⁾ to prepare imidazolato-complexes of first row transition metals employing transition metal salts and imidazole in aqueous media in the presence of KOH have yielded polymeric substances which neither melt nor dissolve in any solvent. We have, however, observed that trimethylsilylimidazole and trimethylsilyl-2-methylimidazole are suitable reagents for the synthesis of monomeric imidazolato-complexes which melt sharply and are soluble in most non-polar organic solvents. The reaction of the trimethylsilyl group in trimethylsilylimidazole towards C—Cl bonds to form the corresponding *N*-substituted imidazole derivatives is quite well known^(2,3). However, to our knowledge, no report has appeared⁽⁴⁾ in the literature regarding the reactivity of trimethylsilylimidazole towards M—Cl bonds of first row transition metal chlorides or of their complexes. It has recently, been reported⁽⁵⁾ that $(\text{Me}_3\text{SiN})_2\text{S}$ reacts with VCl_4 , VOCl_3 or WCl_6 producing metalla-cycles $(\text{Cl}_n\text{MS}_2\text{N}_3)_x$, with delocalized π -electrons.

We here report the reactions of *N*-trimethylsilylimidazole and *N*-trimethylsilyl-2-methylimidazole with anhydrous CoCl_2 and $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ affording (1)–(4). The physico-chemical data presented here suggest that these compounds are examples of uncommon two-coordinate cobalt(II) derivatives. Another known example⁽⁶⁾ of this kind is bis[di(trimethylsilyl)amino]-cobalt(II).

Results and discussion

The elemental analyses and stoichiometries of the products are indicated in Table 1 or the reactions of CoCl_2 with trimethylsilylimidazole, and trimethylsilyl-2-methylimidazole, the final product in each case has been characterized as $[\text{CoLCl}]$ (L = imidazolato or 2-methylimidazolato) even though the silyl reagents were in excess (1:2.8) to that required for the total removal of chlorine as Me_3SiCl .



There is no indication of even traces of metallic cobalt in either reaction, as has been reported⁽⁷⁾ for the reaction of LiNEt_2 with CoCl_2 .

Reactions of $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ with the reagents release all the Ph_3P (experimental section). It is surprising that Ph_3P , a strong π -acid, is liberated⁽⁸⁾. This has been further substantiated by the observation that the attempt to obtain $[\text{Co}(\text{Ph}_3\text{P})_n\text{L}_2]$ ($n = 1$ or 2) by reaction of (3) and (4) with Ph_3P in tetrahydrofuran (THF) leads to the isolation of unreacted starting materials. The analogous compound $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$, prepared by Burger *et al.*⁽⁶⁾, also does not form a complex with tetrahydrofuran, a strong σ donor. However, the reaction of $\text{LiN}(\text{Me}_3\text{Si})_2$ with $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ is reported⁽⁹⁾ to yield the complex $[\text{Co}(\text{Ph}_3\text{P})\{\text{N}(\text{Me}_3\text{Si})_2\}_2]$, in which the π -acceptor properties of Ph_3P are supposed to play an important role.

The complexes are sensitive to air, turning to dark blue sticky liquids and are readily solvolyzed by water and alcohol, forming pink solutions. They are fairly soluble in

Table 1. Elemental analyses of the complexes

Complexes	Found (Calcd) %				M.Wt Found (Calcd)
	C	H	N	Cl	
$[\text{Co}(\text{Iz})\text{Cl}]$	22.2	1.6	17.3	36.0	208
	(22.3)	(1.9)	(17.4)	(36.5)	(220)
$[\text{Co}(\text{MeIz})\text{Cl}]$	27.8	2.5	15.4	32.7	200
	(27.4)	(2.9)	(16.0)	(33.6)	(202)
$[\text{Co}(\text{Iz})_2]$	28.5	2.4	22.1	45.4	208
	(28.6)	(2.4)	(22.2)	(46.8)	(193)
$[\text{Co}(\text{MeIz})_2]$	34.2	3.3	19.9	41.8	233
	(34.3)	(3.6)	(20.0)	(42.1)	(220)

Iz = imidazolato, MeIz = methylimidazolato.

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Table 2 Imidazole ring $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ frequencies (cm^{-1})

Complexes	R_1	R_2	R_3	R_4	M-N	M-Cl
[Co(Iz)Cl]	1545s	1480m	1420s	1345m	385s	325m
[Co(MeIz)Cl]	1565s	1480m	1420s	1330m	390s	320m
[Co(Iz) ₂]	1555s	1475m	1425s	1350m	385s	
[Co(MeIz) ₂]	1540s	1490m	1420s	1335s	375s	

Table 3. μ_{eff} (B.M.), reflectance and electronic spectra (cm^{-1}) and their assignments

Assignment	[Co(Iz)Cl]*	[Co(MeIz)Cl]*	[Co(Iz) ₂]*	[Co(MeIz) ₂]*
CT	40800 30300 (40200 31260)	40520, 30780 (41120, 32260)	40550, 30280 (41270, 31260)	40500 30300 (41030 30800)
$^4T_1(P) \leftarrow ^4A_1(F)$	23220 (22410)	23300 (22500)	23200 (22500)	23480 (23200)
$^4T_2(P) \leftarrow ^4A_1(F)$	16600 (16000)	16670 (16130)	16550 (16250)	16800 (15760)
$^4A_1(F) \leftarrow ^4A_1(F)$	11500 (11980)	11360 (12310)	11360 (11790)	11560 (11790)
μ_{eff}	4.72	4.68	4.52	4.60

*Positions in CH_2Cl_2 solution given in parentheses

most non-polar organic solvents. The molecular weights in (Table 1) suggest that all these compounds are essentially monomeric in solution.

The characteristic *ir* imidazole ring vibrations (Table 2) are slightly shifted ($10\text{--}20\text{ cm}^{-1}$) from the position in the free imidazole, similar to the spectra of transition metal imidazolato-complexes⁽¹⁰⁻¹¹⁾ and of $[\text{BH}_{4-n}\text{L}_n]^-$ ($n = 2, 3$ or 4 , $\text{L} = \text{imidazolate}$ and 2-methyl-imidazolate). A band at about 390 cm^{-1} is attributed to $\nu(\text{M}-\text{N})$ of $\nu(\text{M}-\text{N})$ in imidazolato-complexes appears⁽¹⁰⁾ at $\text{ca } 250\text{ cm}^{-1}$. In $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\text{M} = \text{Co}, \text{Zn}, \text{Cd}, \text{ or } \text{Hg}$) $\nu(\text{M}-\text{N})$ occurs at $\text{ca } 390\text{ cm}^{-1}$ ^(15, 6, 12), attributed to the π -donor nature of the ligand. The same may be true in the present complexes. The imidazolato-moiety in the present complexes could be acting as a four-electron donor (σ and π). The band of medium intensity at about 320 cm^{-1} arising in (1) and (2) is assigned⁽¹³⁾ to $\nu(\text{M}-\text{Cl})$.

The electronic spectra in CH_2Cl_2 (Table 3) are identical to the reflectance spectra of the solids, indicating the existence of similar species in solution as well as in the solid. The peaks are reasonably assignable to transitions characteristic of a linear arrangement⁽¹⁴⁾ of ligands around cobalt(II) in D_{2h} symmetry, similar to that reported⁽¹⁵⁾ for gaseous CoCl_2 . The electronic spectra in THF are, however, different, containing a strong band at 15000 cm^{-1} with a shoulder at $\text{ca } 17000\text{ cm}^{-1}$, attributable to tetrahedral geometry⁽¹⁶⁾ around cobalt(II). This change from linear in the solid and in CH_2Cl_2 solution to tetrahedral in THF solution may be due to coordination of THF in solution, which does not seem uncommon in view of a strong donor capacity⁽¹⁷⁾ of THF. Solutions in methanol and ethanol have a pink colour and visible spectra consistent with an octahedral geometry⁽¹⁸⁾ for the solvolysis product.

The observed magnetic moment values (Table 3) are consistent with a high-spin d^7 system⁽¹⁹⁾. As suggested earlier^(6, 14, 15), the ligand field of two nitrogens in a linear arrangement should not be large enough to allow the mixing of non degenerate excited states, resulting in a higher μ_{eff} value than the theoretical spin-only value.

Experimental

The reagents used, Ph_3P , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, imidazole, 2-methylimidazole, and hexamethyldisilazane were commercially pure samples. The solvents THF, CH_2Cl_2 , petroleum ether, *n*-hexane, CHCl_3 and PhH, were dried by literature methods⁽²⁰⁾. CoCl_2 was dehydrated⁽²¹⁾ and $[\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ was prepared by the reported methods⁽²²⁾ and checked by elemental analyses and *ir*. Trimethylsilylimidazole was prepared as reported elsewhere⁽²³⁾. Trimethylsilyl-2-methylimidazole was prepared in an analogous manner and the fraction distilling at 180°C and 20 torr were collected. Found: $\text{C } 54.5\%$, $\text{H } 9.1\%$, $\text{Si } 18.1\%$, calcd: $\text{C}_7\text{H}_{14}\text{SiN}_2$, $\text{C}, 54.50\%$, $\text{H}, 9.3\%$, $\text{N}, 18.2\%$. *Ir*: $3200\text{--}2900\text{ sb}$, 1600 m , 1570 m , 1480 m , 1400 s , 1290 s , 1255 s , 1180 s , 1150 s , 1050 s , 985 s , 850 sb , 760 s , 745 s , 650 s , 620 s cm^{-1} , $^1\text{H nmr}$, 0.39δ (8 H), 2.38δ (3 H) and 6.8δ (2 H).

Preparation of chloro(imidazolato)cobalt(II) and chloro(2-methylimidazolato)cobalt(II) (1) and (2)

N-trimethylsilylimidazole or *N*-trimethylsilyl-2-methylimidazole (2.94 mmol) diluted with PhH (30 cm^3) was added dropwise to a round-bottomed flask containing CoCl_2 (1.05 mmol) suspended in PhH (30 cm^3), with continuous magnetic stirring at room temperature under dry N_2 atmosphere. A light blue oil immediately formed and the reaction mixture was stirred for $\text{ca } 0.5\text{ h}$. The mother liquor was decanted, leaving an oily mass which was washed several times with petroleum ether and vacuum dried giving a microcrystalline solid [m.p. 125°C for (1) and 98°C for (2)]. The crude product was dissolved in CH_2Cl_2 (50 cm^3), filtered to remove impurity, mixed with *n*-hexane and kept at 5°C for about two weeks. This gave light blue hexagonal crystals [m.p. 130°C for (1) and 102°C for (2)].

Preparation of bis(imidazolato)cobalt(II) (3) and bis(2-methylimidazolato)cobalt(II) (4)

Trimethylsilylimidazole (1.28 g, 9.2 mmol) diluted with

PhH (30 cm³) was added dropwise to [Co(Ph₃P)₂Cl₂] (3.00 g, 4.6 mmol) dissolved in THF (200 cm³) with continuous stirring at room temperature under dry N₂ atmosphere. When all the Me₃Si imidazole had been added (ca. 30 min) the reaction mixture was vigorously stirred for an additional 0.5 h and left standing for 1 h. The colourless mother liquor was decanted leaving a blue oil, which was immediately washed with PhH. THF mixture then with petroleum ether and the washings were mixed to the filtrate mother liquor. The mass was vacuum dried and 2.02 g of a light blue amorphous solid (m.p. 135–145°C) were obtained. The mother liquor was vacuum dried giving 2.3 g of a colourless microcrystalline material (m.p. 79–82°C) which has been identified as Ph₃P from i.r. and elemental analysis. The main product was recrystallized in CH₂Cl₂/n-hexane giving a microcrystalline solid melting at 147°C.

Bis(2-methylimidazolato)cobalt(II) was synthesized in the same manner by taking (0.45 g, 2.9 mmol) trimethylsilyl-2-methylimidazole in PhH (20 cm³) and (0.685 g, 1.05 mmol) [Co(Ph₃P)₂Cl₂] in THF (60 cm³) at room temperature. The crude was recrystallized from CH₂Cl₂/n-hexane giving a blue microcrystalline solid (m.p. 130°C). As before the mother liquor and washings afforded 0.55 g Ph₃P.

The elemental analyses were obtained by the Micro analytical Laboratory of the Indian Institute of Technology Kanpur. Cobalt and chloride were estimated by EDTA titration⁽²⁴⁾ and gravimetrically⁽²⁵⁾, respectively. I.r. spectra (4000–200 cm⁻¹) were recorded as KBr discs on a Perkin Elmer 621 spectrophotometer. Reflectance spectra of solid samples in MgO were recorded on Carl-Zeiss VSU-2P spectrophotometer. Electronic spectra in CH₂Cl₂, THF or MeOH were recorded on Pye Unicam 8800 spectrophotometer at room temperature. ¹H n.m.r. spectra were recorded in CDCl₃ on a Varian A60D spectrometer using Me₄Si as an internal indicator. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. Molecular weights were determined by the Rast method⁽²⁶⁾ using camphor as a solvent.

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References

- J. E. Bauman Jr and J. C. Wang *Inorg. Chem.* **3**, 368 (1964).
- W. J. Eilbeck, F. Holmes and A. E. Underhill *J. Chem. Soc. (A)* 757 (1967).
- L. Birkofer, P. Richter and A. Ritter *Chem. Ber.* **99**, 2804–2810 (1960).
- H. A. Stabb *Chem. Ber.* **89**, 1927 (1956).
- R. Weiss *et al.* *Inorg. Chem.* **26**, 1189 (1987) have mentioned the reaction of Mn(IV) oxoporphyrin derivatives with Me₃Si imidazole yielding a Mn^{III} dimidazolato complex whose precise nature is under investigation.
- J. Anhaus, Z. A. Siddiqi, J. Schimkowiak and H. W. Roesky *Z. Naturforsch.* **39B**, 1722 (1984).
- H. Burger and U. Wannagat *Monatsh. Chem.* **94**, 1007 (1963); *ibid.* **95**, 1099 (1964); D. C. Bradley and K. J. Fisher *J. Am. Chem. Soc.* **93**, 2058 (1971).
- R. Bonnett, D. C. Bradley and K. J. Fisher *Chem. Commun.* 1967 (1968); *J. Chem. Soc. (A)*, 1622 (1971).
- In the similar reactions of [(PPh₃)₂NiCl₂] with silylimidazoles we have observed that the final products do not contain any coordinated PPh₃.
- D. C. Bradley, M. B. Hursthouse, R. J. Smallwood and A. J. Welch *Chem. Commun.* 872 (1972).
- J. Reedijk *Rec. Trav. Chim.* **88**, 1451 (1969).
- S. A. A. Zaidi, T. A. Khan and Z. A. Siddiqi *Synth. React. Inorg. Met. Org. Chem.* **4**, 717 (1984); *Bull. Soc. Chim. Fr.* **5–6**, 149 (1984).
- H. Burger, W. Sawodny and U. Wannagat *J. Organometal. Chem.* **3**, 113 (1965).
- R. J. H. Clark and C. S. Williams *Inorg. Chem.* **4**, 350 (1965).
- Andrew D. Liehr *J. Chem. Educ.* **39**, 135 (1962).
- J. T. Hogen, G. E. Leroi and T. C. James *J. Chem. Phys.* **34**, 1670 (1961); C. W. DeKock and D. M. Gruen *ibid.* **44**, 4387 (1966).
- F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco *J. Am. Chem. Soc.* **83**, 4157 (1961).
- D. C. Bradley *Chem. Brit.* **11**, 393 (1975).
- C. J. Ballhausen *Introduction to Ligand Field Theory*, McGraw-Hill Book Co. Inc. Corp. Ltd. New York, Chapter X, 1962.
- B. N. Figgis and J. Lewis *Modern Coordination Chemistry*, J. Lewis and R. G. Wilkins (Eds.), Interscience, New York, Chapter VI, 1960.
- A. E. Vogel *Textbook of Practical Organic Chemistry*, IV Edit., Chapter II, 1978.
- G. Brauer *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York, London, **2**, 1515 (1965).
- H. A. Tayim, A. Bouldoukian and F. Awad *J. Inorg. Nucl. Chem.* **32**, 3799 (1970).
- D. A. Armitage, M. J. Clark, A. W. Sinden, J. N. Wingfield, K. W. Abel (Sec. B and C) and E. J. Louis (Sec. A) *Inorganic Synthesis*, McGraw-Hill Book Co., New York, Vol. XV, 207, 1974.
- C. N. Reilly, R. W. Schmid and F. A. Sadak *J. Chem. Educ.* **36**, 619 (1959).
- I. M. Kolthoff, E. B. Sandell, L. J. Meehan and S. Bruckenstein *Quantitative Chemical Analysis*, MacMillan, London, p. 580, 1969.
- F. G. Mann and B. C. Saunders *Practical Organic Chemistry*, Longmans, London, 435, 1961.

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Reactivity of *N*-trimethylsilylimidazole and 2-methylimidazole; synthesis and physico-chemical studies on transition metal imidazoles and mixed ligand imidazoles

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Summary

N-trimethylsilylimidazole and *N*-trimethylsilyl-2-methylimidazole react with MCl_2 to yield $[ML_2]$ ($M = Ni$ or Cu , $L =$ imidazole or 2-methylimidazole). The complex $[NiL_2]$ can also be prepared from $[Ni(Ph_3P)_2Cl_2]$. $[Cu(Ph_3P)_3Cl]$ yields $[Cu(Ph_3P)_2L]$. The complexes are soluble in most non-polar organic solvents and experimentally determined molecular weights suggest they are monomers in solution. Magnetic susceptibility measurements and reflectance and electronic spectral studies at room temperature are commensurate with square-planar geometry for $[CuL_2]$. Although, the ligand field spectrum for $[NiL_2]$ is compatible with a square-planar geometry, the anomalous μ_{eff} value suggests that the ground electronic state of Ni^{II} in $[NiL_2]$ is near the magnetic cross-over point concomitant with the singlet-triplet spin state equilibrium. The IR spectra exhibit characteristic imidazole and Ph_3P ring vibrations, and $\nu(M-N)$ and $\nu(M-P)$ stretching vibrations at the appropriate frequencies. The synthesis and characterization of a Cu^{II} complex, formulated as $[Cu(Ph_3P)_2LCl]$, with tetrahedral structure is described.

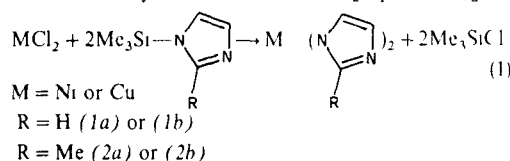
Introduction

The reactivity of the trimethylsilyl group in *N*-trimethylsilylimidazole towards $C-Cl$ bonds has been well exploited for the preparation⁽¹⁾ of *N*-substituted imidazoles. A study of analogous reactions involving $M-Cl$ substrates bond has been initiated, recently⁽²⁾, by us. $CoCl_2$ and the complex $[Co(Ph_3P)_2Cl_2]$ yielding⁽²⁾ monomeric $[CoLCl]$ and $[CoL_2]$ respectively, in which the imidazole moiety is covalently bonded, with appreciable π donation, to cobalt(II). We thought it worthwhile to study the reactivity of the *N*-silylimidazole reagent towards various transition metal chlorides and their complexes with a view to using it to prepare monomeric imidazoles as well as mixed-ligand imidazoles. This paper describes the reactions of *N*-trimethylsilylimidazole and *N*-trimethylsilyl-2-methylimidazole with $NiCl_2$, $[Ni(Ph_3P)_2Cl_2]$, $CuCl_2$ and $[Cu(Ph_3P)_3Cl]$ yielding (1a)–(3b). Reactions of $CuCl_2$ with Ph_3P together with the reagents yield a blue amorphous solid and the physico-chemical investigations presented here, suggest it is $[Cu(Ph_3P)_2LCl]$ with a probable tetrahedral array of ligands around the metal ion (d^9 configuration).

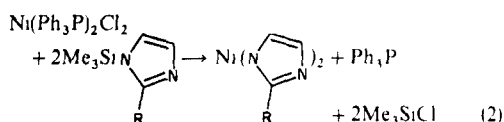
Results and discussion

The observed reactivity of *N*-trimethylsilylimidazole and *N*-trimethylsilyl-2-methylimidazole towards transition metal chlorides and their complexes is reasonably ascribed to the affinity of the Me_3Si- group for chlorine in

the substrate, leading to release of Me_3SiCl . The results of the elemental analyses and the experimentally determined molecular weight of the final products of the various reactions are given in Table I. For the reactions of anhydrous $NiCl_2$ or $CuCl_2$ with trimethylsilylimidazole or 2-methylimidazole, the product, in each case, has been identified as $[ML_2]$, suggesting the replacement of both the chlorines by imidazole moieties [Equation (1)].

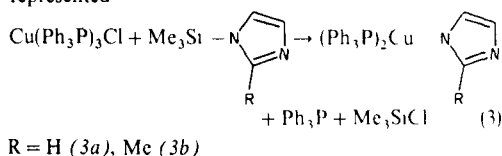


However, under similar conditions⁽²⁾, $CoCl_2$ yields $[CoLCl]$. $[NiL_2]$ has also been obtained quantitatively when $[Ni(Ph_3P)_2Cl_2]$ is reacted with the reagent [Equation (2)].



The π acceptor properties of Ph_3P in the precursor usually plays an important role and is assumed to be generally operative⁽³⁾ in most of its reactions. However, in the reactions under discussion no such generalization is possible. A similar mode of reaction for $[Co(Ph_3P)_2Cl_2]$ is apparent⁽²⁾.

The reaction with the precursor $[Cu(Ph_3P)_3Cl]$ liberates one mole equivalent of Ph_3P and yields $[Cu(Ph_3P)_2L]$. The reaction in this case may be represented



The reaction of $CuCl_2$ with Ph_3P is known to yield⁽⁴⁾ a copper(I) complex. However, under our conditions, it has been performed in the presence of trimethylsilylimidazole or 2-methylimidazole. The final products in either case have the stoichiometry $[Cu(Ph_3P)_2LCl]$ (4a) or (4b). The physico-chemical investigations *vide infra* agree with a d^9 configuration for copper with a tetrahedral ligand array.

All complexes are soluble in most organic solvents, are moisture sensitive and are hydrolysed by water. The experimentally determined molecular weight agrees with a monomeric structure. The important characteristic imidazole and Ph_3P ring vibrations, as well as $\nu(M-N)$, $\nu(M-P)$ and $\nu(M-Cl)$, stretching vibrations in the

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Table 1 Elemental analyses of the imidazole complexes

Complex		Found (Calcd) %					Mol. wt found (Calcd)
		C	H	N	M	Cl	
[Ni(Iz) ₂]	(1a)	37.0 (37.4)	3.0 (3.1)	28.8 (29.1)	29.5 (30.5)		182 (193)
[Ni(MeIz) ₂]	(1b)	43.1 (43.5)	4.3 (4.5)	24.9 (25.4)	25.2 (26.6)		208 (221)
[Ni(Iz) ₂]*	(1a)	37.1 (37.4)	3.0 (3.1)	28.9 (29.1)	29.4 (30.5)		180 (193)
[Ni(MeIz) ₂]*	(1b)	43.3 (43.5)	4.2 (4.5)	25.1 (25.4)	25.8 (26.6)	-	230 (221)
[Cu(Iz) ₂]	(2a)	36.1 (36.5)	3.0 (3.0)	27.8 (28.3)	30.9 (32.2)		205 (198)
[Cu(Ph ₃ P) ₂ (Iz)]	(3a)	70.9 (71.5)	4.9 (5.0)	4.0 (4.3)	8.4 (9.7)		635 (655)
[Cu(Ph ₃ P) ₂ (MeIz)]	(3b)	70.8 (71.8)	5.0 (5.2)	4.1 (4.2)	8.5 (9.5)		650 (669)
[Cu(Ph ₃ P) ₂ (Iz)Cl]	(4a)	67.3 (67.8)	4.7 (4.8)	3.9 (4.1)	7.8 (9.2)	4.7 (5.2)	678 (690)
[Cu(Ph ₃ P) ₂ (MeIz)Cl]	(4b)	68.0 (68.2)	4.9 (5.0)	3.7 (4.0)	8.1 (9.0)	4.2 (5.0)	715 (704)
[Cu(MeIz) ₂]	(2b)	42.0 (42.6)	3.9 (4.4)	24.2 (24.8)	27.0 (28.2)		235 (226)

Iz = Imidazolate; MeIz = methylimidazolate *obtained after following the reaction shown by Equation (2) (See text)

IR spectra of the various complexes are summarized in Table 2 which shows that some of the characteristic imidazolate ring vibration bands overlap with that of the Ph₃P. Nevertheless, bands which are diagnostic for imidazolate and/or Ph₃P are clearly indicated^(5,6). The absence of a strong band at *ca* 500 cm⁻¹ (characteristic of Ph₃P) in (1a) and (1b) confirms the mode of reaction, Equation (2). The band of medium to strong intensity, observed in the 370–390 cm⁻¹ region is assigned to $\nu(\text{M}—\text{N})$. The nature and position of this band is similar to that observed⁽²⁾ for bis(imidazolato)cobalt(II) or bis(2-methylimidazolato)cobalt(II) and lies in the range reported⁽⁷⁾ or bis{di(trimethylsilyl)amino} cobalt(II), zinc(II) or cadmium(II). The $\nu(\text{M}—\text{P})$ and $\nu(\text{M}—\text{Cl})$ stretching vibrations are indicated at the appropriate positions^(6,8).

The electronic spectra (non-polar solvent) are nearly identical to the reflectance spectra of the solids (Table 3), indicating the presence of similar species in the solution as well as in the solid. The band positions observed in (1a) and (1b) are characteristic of a diamagnetic square-planar nickel(II) complex⁽⁹⁾. However, the observed (Table 3) abnormal magnitude, μ_{eff} (*ca* 1.0 μ_B) favours paramagnetism in the complex. The ground electronic state of nickel(II) complexes (singlet diamagnetic or triplet paramagnetic) are exceptionally sensitive to geometry and or to the ligand field^(10a,b) strength. The square-planar nickel(II) complexes are generally considered to be diamagnetic (singlet ground state ¹A_{1g}). However, the ligand field treatment by Ballhausen and Liehr^(10b) suggests that the square-planar configuration may be retained even in triplet ground state. It is, quite possible, that [NiL₂] is sq-pl with ¹A_{1g} ground state but mixed with or in equilibrium with paramagnetic species with triplet ground state. A linear geometry with D_{∞h} symmetry, possessing a triplet ground state⁽¹¹⁾, as reported to exist in free gaseous NiCl₂, may be invoked for [NiL₂]. The characteristic ligand field transitions for this highly paramagnetic d⁸ system appear⁽¹¹⁾ at 13000 and

21700 cm⁻¹ which are in close proximity to the two lower energy bands (Table 3) of the sq-pl configuration. The pyridyl nitrogen of the imidazole moiety is known⁽⁶⁾ to be basic enough to coordinate metal ions. In [NiL₂] too which appears to be coordinatively unsaturated, interaction of the pyridyl nitrogen is apparently significant even in solution, leading to the observed square planar geometry. A spin state isomerism^(12,13) may also be visualized. In other words, the energy levels of different multiplicities are positioned with kT of each other making the complex near the magnetic cross-over point whereby population of both states become equally probable.

The broad band appearing at *ca* 14000 cm⁻¹ in the ligand field spectrum of (2a) and (2b) is assignable to the envelope of transitions ²A_{1g}, ²B_{2g}, ²E_g ← ²B_{1g} characteristic of square-planar geometry⁽¹⁴⁾. The observed μ_{eff} value is consistent with a d⁹ configuration of copper.

The μ_{eff} values for (4a) and (4b) are some-what higher from the calculated spin-only value (S = 1/2) as expected owing to the spin-orbit coupling contribution however they lie in the range normally observed for various copper(II) complexes⁽¹⁵⁾. The electronic spectra show a weak broad band at *ca* 22000 cm⁻¹ in addition to the charge-transfer bands in the 45000–35000 cm⁻¹ region. The former weak band may be assigned to the blank⁽⁹⁾ of the tetrahedrally coordinated copper(II) ion which is generally indicated in 10000–20000 cm⁻¹ region. The main d-d band expected in the near IR region could not be recorded as it lies beyond the range of our instrument. A regular tetrahedral geometry, in view of well-known reasons^(15,16), is unjustified, rather a flattening⁽¹⁶⁾ from regular tetrahedral geometry do occur in some cases. In (4a) and (4b), presumably the steric factor predominates and leads preferentially to a tetrahedral structure^(15,17). Our data rule out any possibility for the formation of a reduced i.e. copper(I) species [i.e. reaction of CuCl₂ with Ph₃P invariably yields⁽⁴⁾ a copper(I) complex]. Furthermore, the products contain one chlorine (vide *supra*) even-though, the reagents present in sufficient quantity to

Table 2. Imidazole- and Ph_3P ring, $\text{M} \cdots \text{N}$, $\text{M} \cdots \text{P}$, and $\text{M} \cdots \text{Cl}$ frequencies (cm^{-1}).

Complexes	Imidazole	Ph_3P	$\text{M} \cdots \text{N}$	$\text{M} \cdots \text{Cl}$	$\text{M} \cdots \text{P}$
(1a)	1550s, 1480m, 1420s, 1340m;	—	390s	—	—
(1b)	1570s, 1470m, 1420s, 1320m;	—	390s	—	—
(2a)	1555s, 1475m, 1430s, 1320m;	—	375s	—	—
(2b)	1550s, 1480m, 1420s, 1340m;	—	375s	—	—
(3a)	1550s, 1480s, 1430s, 1320m;	1480s, 1430s, 1090s, 740s, 720s, 510s, 500s	370m	—	320w
(3b)	1550s, 1475s, 1430s, 1345m.	1475s, 1430s, 1100s, 750s, 720s, 510s, 490s	380m	—	310w
(4a)	1530s, 1480s, 1420s, 1320m;	1480s, 1420s, 1090s, 740s, 700s, 510s, 490s	370m	270m	330w
(4b)	1550s, 1475s, 1430s, 1350m;	1475s, 1430s, 1090s, 740s, 700s, 510s, 490s	375m	270m	310w

Table 3. μ_{eff} (B.M.)^a and ligand field bands observed in the reflectance and electronic spectra in cm^{-1} and their assignments.

Complex	μ_{eff}	Band position	Assignment
(1a)	0.9	30300(29500)	$^1B_{1g} \leftarrow ^1A_{1g}$
		23800(23300)	$^1A_{2g} \leftarrow$
		14280(14500)	$^3A_{2g} \leftarrow$
(1b)	1.1	30350(30300)	$^1B_{1g} \leftarrow ^1A_{1g}$
		23620(23500)	$^1A_{2g} \leftarrow$
		14140(14000)	$^3A_{2g} \leftarrow$
(2a)	1.86	14500(14300)	$^2A_{1g}, ^2B_{2g}, ^2E_g \leftarrow ^2B_{1g}$
(2b)	1.91	14260(14100)	$^2A_{1g}, ^2B_{2g}, ^2E_g \leftarrow ^2B_{1g}$
(4a)	1.93	22700(22200)	blank
(4b)	1.91	22000(21700)	blank

Positions in CH_2Cl_2 solution given in parentheses. ^aNon SI unit employed $\text{B.M.} = 0.9274 \times 10^{-23} \text{ JT}^{-1}$

cause the replacement of both the chlorines. Steric factor may be assumed to be operative in restricting the further substitution. The same argument seems valid to account for the release of one mole of Ph_3P from the reaction of $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$ with the reagents corroborating the reaction given by Equation (3). In the absence of any spectral and magnetic data, and view of the analogy of the copper(II) complex, we assume that (3a) and (3b) are tetrahedral.

Experimental

Ph_3P , $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (all B.D.H.), imidazole, 2-methylimidazole, $(\text{Me}_3\text{Si})_2\text{NH}$ (all E. Merck) were commercially pure samples. Metal salts were dehydrated and the precursors $[\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ prepared by reported methods⁽¹⁸⁾, were checked by i.r. and elemental analyses. Solvents were dried before use. *N*-trimethylsilylimidazole was prepared as reported⁽¹⁹⁾. The preparation of *N*-trimethylsilyl-2-methylimidazole has been described elsewhere⁽²⁾. The purity of the reagents was checked by i.r. and ^1H n.m.r.

Reactions of N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole with MCl_2 [$\text{M} = \text{Ni}$ (1a) or (1b); Cu (2a) or (2b)]

Trimethylsilyl-imidazole or -2-methylimidazole (5.0 mmol) diluted in THF (50 cm^3) was dropped to the suspension of metal salts (2.5 mmol) in THF (150 cm^3) with continuous stirring in a dry N_2 atmosphere at RT. The reaction mixture was first stirred for an additional ca. 1 h then filtered to remove the unreacted salt impurity (only traces). The solid was dried *in vacuo*, washed several times with light petrol to leave a moisture sensitive amorphous solid which was recrystallised from CH_2Cl_2 -*n*-hexane [M.ps. (1a) 190°C, (1b) 200°C; (2a) 180°C, (2b) 210°C].

Reactions of *N*-trimethylsilylimidazole or *N*-trimethylsilyl-2-methylimidazole with $[Ni(Ph_3P)_2Cl_2]$ to give bis(imidazolato)nickel(II) (1a) or bis(2-methylimidazolato)nickel(II) (1b)

The diluted reagent (4.0 mmol) in THF (40 cm³) was dropped to the solution of the precursor (2.0 mmol) in THF (100 cm³) with stirring. The reaction mixture was vacuum dried as above giving a light green oily mass which was washed repeatedly with light petrol changing to pea-green amorphous solid. The crude was recrystallised as above [Mps same as of (1a) or (1b)]. The petrol washing on evaporation under vacuum left a colourless microcrystalline mass (ca. 1.0 gm i.e. 2.0 mmol equivalent) which has been identified as Ph_3P from m.p. i.r. and microanalyses.

Reactions of *N*-trimethylsilylimidazole or *N*-trimethylsilyl-2-methylimidazole with $[Cu(Ph_3P)_3Cl]$ to give imidazolato bis(triphenyl phosphine) copper(I) (3a) or 2-methylimidazolato bis(triphenyl phosphine) copper(I) (3b)

Reactions have been performed separately by taking equimolar (1.9 mmol) solutions of the precursors and the reagents in THF as above. A curdy white precipitate is immediately formed which during stirring slowly dissolved in the mother liquor. It was dried under reduced pressure washed as above and vacuum dried. The crude was recrystallised from CH_2Cl_2 -*n*-hexane giving colourless microcrystalline solid [Mps (3a) 185°C, (3b) 195°C]. Here too washings have yielded liberated Ph_3P (ca. 1.9 mmol equivalent).

Chloro(imidazolato)bis(triphenyl phosphine)copper(II) (4a) chloro(2-methylimidazolato)bis(triphenyl phosphine)copper(II) (4b)

To a suspension of $CuCl_2$ (2.5 mmol) in THF (80 cm³), solutions of Ph_3P (5.0 mmol) and the reagent trimethylsilyl-imidazole or -2-methylimidazole (5.0 mmol) both in THF (50 cm³) taken in separate dropping funnels, were simultaneously dropped at a slow rate with continuous stirring at RT. The reaction mixture was stirred for an additional ca. 2 h after the whole of the reactants have been added, filtered to remove the unreacted $CuCl_2$. The mother liquor was vacuum dried and washed with ether, the crude was recrystallised from CH_2Cl_2 -*n*-hexane [Mps (4a) 215°C (4b) 185°C].

The elemental analyses were obtained by micro-analytical laboratory of the Indian Institute of Technology Kanpur. Metals and chlorides were estimated by EDTA⁽²⁰⁾ titration and gravimetrically⁽²¹⁾ respectively. I.r. spectra (4000–200 cm⁻¹) were recorded as KBr discs on a Perkin-Elmer 621 spectrophotometer. Reflectance spectra of solid samples in MgO were recorded on Carl-Zeiss VSU 2P spectrophotometer and electronic spectra CH_2Cl_2 solutions were recorded on Pye Unicam 8800 spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using Faraday balance at 25°C. Molecular weights of the compounds

were determined using camphor as solvent by Rast method⁽²²⁾.

Acknowledgement

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References

- (1) H. A. Stark, *Chem. Ber.* **89**, 1927 (1956); I. Birkhofer, P. Richter and A. Ritter, *Chem. Ber.* **99**, 2804 (1966); *ibid.* **99**, 2810 (1966).
- (2) Z. A. Siddiqi, S. N. Qidwai, M. Jirri and M. Shikri, *Transition Met. Chem.* in press.
- (3) D. C. Bradley, *Chem. Brit.* **11**, 393 (1975).
- (4) G. Booth, *Advan. Inorg. Chem. and Radiochem.* **6**, 1 (1964) and refs therein.
- (5) J. Reedijk, *Rec. Trav. Chim.* **88**, 1451 (1969); S. A. A. Zaidi, T. A. Khan and Z. A. Siddiqi, *Polyhedron* **4**, 1166 (1985) and refs therein.
- (6) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edit. J. Wiley, 1978.
- (7) D. C. Bradley and K. J. Fischer, *J. Amer. Chem. Soc.* **93**, 2958 (1971); H. Burger, W. Siwodny and U. Winnig, *J. Organometal. Chem.* **3**, 113 (1965).
- (8) R. J. H. Clark and C. S. Williams, *Inorg. Chem.* **4**, 350 (1965).
- (9) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Edit. Elsevier, Amsterdam, 1984.
- (10) a) G. Maki, *J. Chem. Phys.* **29**, 1129 (1958); b) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.* **81**, 538 (1959); c) R. H. Holm and T. M. Kinney, *J. Amer. Chem. Soc.* **82**, 5505 (1960); d) J. Ferguson, *J. Chem. Phys.* **34**, 611 (1961); e) W. J. Eilbeck, I. Holms and A. E. Underhill, *J. Chem. Soc. (A)*, 757 (1967).
- (11) A. D. Liehr, *J. Chem. Educ.* **39**, 135 (1962); J. T. Hougen, G. E. Leroy and T. C. James, *J. Chem. Phys.* **34**, 1670 (1961).
- (12) R. H. Holm and K. Swaminathan, *Inorg. Chem.* **2**, 181 (1963).
- (13) R. H. Holm, *J. Amer. Chem. Soc.* **82**, 5632 (1960).
- (14) I. M. Proctor, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. (A)*, 1678 (1968); A. Longo and I. Buch, *Inorg. Chem.* **6**, 556 (1967).
- (15) B. N. Figgis and J. Lewis, *Progr. in Inorg. Chem.* **6**, 37 (1964).
- (16) B. Morosin and E. C. Lingafelter, *Acta Crystallogr.* **13**, 807 (1960).
- (17) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 7298 (1961).
- (18) H. A. Tayim, A. Bouldoukian and F. Awad, *J. Inorg. Nucl. Chem.* **32**, 3799 (1970).
- (19) D. A. Armitage, H. J. Clark, A. W. Sindon, J. N. Winfield, E. W. Abel and E. J. Louis (Section A), *Inorganic Syntheses*, McGraw Hill Book Co., New York, **A1**, 207, 1974.
- (20) C. N. Reilly, R. W. Schmid and F. A. Sadak, *J. Chem. Educ.* **36**, 619 (1959).
- (21) A. I. Vogel, *Textbook of Practical Organic Chemistry*, 4 Edit. Ch. 2, 1978.
- (22) F. G. Mann and B. C. Stunders, *Practical Organic Chemistry*, Longmans, London, 435, 1961.

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Synthesis of Bis(imidazolato)dialkyltin(IV) and Covalent Tin(II) Imidazolate Derivatives†

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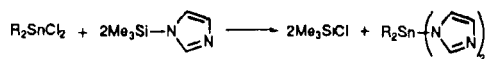
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The preparations of bis(imidazolato)dialkyltin(IV) R_2SnIz_2 (**1** ($R = Me$) and **2** ($R = Bu^n$), $Iz = imidazolate$) and bis(imidazolato)dichlorotin(II) $[SnClIz]_2$ (**3**) are described. Reaction of **1** or **2** with an excess of Ph_3P in refluxing CH_2Cl_2 affords the adduct $[SnIz_2 \cdot Ph_3P]$ (**4**) which undergoes an oxidative addition reaction with 1 mol equiv. of iodine to produce $[SnI_2Iz_2]$ with complete liberation of free Ph_3P .

It is well known that condensation of imidazole with organotin(IV) oxide R_2SnO produces R_2SnIz_2 as the major product. The corresponding R_2SnIz_2 derivatives could not however be isolated utilizing the condensation reaction R_2SnIz_2 being invariably obtained. One of the foremost reasons could be the decomposition of the extremely moisture sensitive R_2SnIz_2 with water released as a by-product in the condensation step to a hydrolytically stable R_2SnIz_2 . We have recently observed that N -trimethylsilylimidazole (Me_3SiIz) is a potent reagent for the preparation of monomeric moisture sensitive transition metal imidazolates in good yields. We henceforth considered it important to exploit this efficient reagent for the preparation of R_2SnIz_2 derivatives. Furthermore, the chemistry of covalent tin(II) derivatives with $Sn^{II}-N$ bonds where N stands for a line or imido group has been extensively investigated, however incorporation of a π -delocalized N -heterocycle, especially in imidazolate ring (4 e^- donor) to a tin(II) centre is described for the first time in this paper.

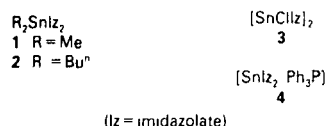
The reagent Me_3SiIz reacted efficiently with R_2SnCl_2 at room temperature producing R_2SnIz_2 (**1** or **2**) in ca. 80% yield. The observed reactivity of the reagent is apparently due to the affinity of the Me_3Si group for chlorine effecting the release of Me_3SiCl similar to that found in its reaction with transition metal chlorides and their complexes as typified by the reaction shown in Scheme 1.



Scheme 1

The compounds were soluble in the usual organic solvents and with the exception of **3** which is a dimer, all behaved as monomers in solution. Their analytic and spectral data are summarised in Table 1. The IR spectra of **1** and **2** contained bands characteristic of an imidazolate moiety in addition to the fundamental bands arising from the organic substituents. Imidazolate ring vibrations designated R_1 , R_2 , R_3 and R_4 were recognizable in the 1600–1300 cm^{-1} region; these are reported to be metal independent and scarcely alter their positions from those observed in free imidazole. The strong band at 535 cm^{-1} was assigned to the $\nu_{as}(Sn^{IV}-N)$ stretching vibration which is similar in position to that reported⁴ for tetrakis(dichthylamido)tin(IV). The 1H NMR spectra of **1** and **2** exhibited signals arising from the imidazolate protons including those arising from organic substituents at appropriate positions. The lone pair at the imine nitrogen of the imidazole moiety may co-ordinate to the tin atom. However intramolecular co-ordination seems sterically improbable and intermolecular co-ordination leading to an octahedral configuration for **1** and **2** appears more favourable.

Reaction of the reagent with $SnCl_2$ produced the dimer $[SnClIz]_2$ (**3**) even though in excess of the reagent was used to ensure exhaustive removal of both the chlorine atoms as Me_3SiCl . A similar observation has also been reported for the reaction between $SnCl_2$ and $Me_3SiEtBu$ ($Et = P$ or As) which yields $[SnClEtBu]_2$. The imidazolate ring vibrations appeared at the expected positions while a band of medium intensity at 410 cm^{-1} could be assigned to the $\nu(Sn^{II}-N)$ stretching vibration which seems reasonable in view of the report⁷ that the $Cd-N$ bond frequency in $Cd[N(SiMe_3)]_2$ also appears in this range. The position of the $Sn^{II}-N$ bond frequency is lower than that of the $Sn^{IV}-N$ bond like that reported⁶ for the corresponding $Sn-O$ bonds. This may be rationalized in terms of the substantial polarity which is expected for the $Sn^{II}-N$ bond which is apparently compatible with the observed medium intensity of this vibration. The $\nu(M-Cl)$ stretching vibration was observed at the reported position (Table 1). The dimer **3** did not show any tendency to transform into the monomeric adduct $[SnClIz \cdot Base]$ as was indicated by the following observations. Treatment of **3** with strong bases such as pyridine, pyridine N -oxide, bipyridine and even Bu_4NI gave only unchanged reactants (identified by physicochemical methods). In order to probe this behaviour of **3** further, the well known $[SnCl_2 \cdot PyNO]$ adduct was chosen as a precursor to react with Me_3SiIz which also afforded the product **3** with the recovery of an equivalent amount of free $PyNO$. This is in contrast to the result reported for bis(dimethylamido)tin(II) and tin(II) diolate⁸ dimers which have been shown to produce 1:1 adducts with bases. This unusual behaviour of **3** may be rationalized in terms of the strong bridging capability provided by the imine nitrogen of the imidazolate moiety resulting in an intact dimer.



Reaction of **1** or **2** with an excess of Ph_3P at the reflux temperature of CH_2Cl_2 under an inert atmosphere proceeded with cleavage of the $Sn-C$ bond to form the adduct $[SnIz_2 \cdot Ph_3P]$ (**4**) in ca. 50% yield. The absence of any alkyl group in the product **4** was confirmed from the spectral data i.e. the 1H NMR spectrum did not show any characteristic methyl or butyl resonances but rather signals characteristic of an imidazolate and a co-ordinated Ph_3P while the IR spectrum showed no characteristic alkyl bands. The 31P NMR spectrum of **4** contained a sharp singlet at δ 4.3 which is in the range reported¹¹ for Ph_3P co-ordinated to metal ions. The cleavage of a $Sn-C$ bond in organotin(IV) derivatives is not a very common feature, however there are a few reports¹¹ that reagents such as PX_3 ($X = \text{halogen}$), $AsCl_3$ and $BiCl_3$ show similar behaviour. We were unable to identify the fate of the alkyl substituents during the course of the reaction.

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This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)* 1990, Issue 1, p. ii]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table Analytical and spectroscopic^a data of compounds **1–5**

Compound	Found (calc.) (%)				Mol wt (calc.)	ν_{max}/cm						δ_H (60 MHz) ^t imidazole protons	
						Imidazole ring vibration							
	C	H	N	M		R	R ₂	R ₃	R ₄	M—N	M—Cl/M—P		
1	30.9 (30.97)	4.2 (4.28)	19.7 (19.80)	41.9 (41.95)	290 (282.91)	1590s	1490m	1410m	1320w	535s	—	7.31 (1 H) 7.50 (2 H)	
2	46.8 (45.81)	6.5 (6.59)	15.2 (15.26)	32.2 (32.33)	352 (367.08)	1600s	1480m	1420s	1310m	535s	—	7.29 (1 H) 7.48 (2 H)	
3	16.2 (16.28)	1.3 (1.37)	12.6 (12.66)	53.5 (53.64)	455 (442.53)	1620m	1480m	1420m	1320s	410m	290m	7.32 (1 H) 7.55 (2 H)	
4	55.9 (55.96)	4.1 (3.11)	10.8 (10.83)	22.9 (23.04)	525 (515.15)	1595s	1475m	1425m	1320s	415m	315w	7.30 (1 H) 7.45 (2 H)	
5	14.3 (14.22)	1.3 (1.18)	11.8 (11.07)	24.05 (23.44)	500 (506.50)	1605s	1485m	1430m	1330s	530s	—	7.25 (1 H) 7.55 (2 H)	

^aIR stretching frequencies and proton resonances of Ph₃P and the alkyl substituent on the tin atom are omitted. In CDCl₃ unless indicated otherwise. In (C₆H₅)₂acetone.

In order to ascertain the stoichiometry of the formation of **4** and to obtain chemical evidence for the oxidation state of the tin atom in the molecule, **4** was subjected to an oxidative addition reaction using an equivalent amount of iodine. A sharp change in the colour of the iodine was observed and the reaction mixture finally afforded an orange microcrystalline product **5** along with free Ph₃P and recovered **4**. Microanalysis verified the stoichiometry of **5** as [SnI₂] and a comparison of the spectral data with those of **4** confirmed the complete liberation of Ph₃P during the course of formation of **5**. The observations indicate that **4** is a genuine tin(II) compound and that the reaction of **1** or **2** with an excess of Ph₃P in refluxing CH₂Cl₂ proceeds through a redox step which may be initiated either by Ph₃P or CH₂Cl₂ or both. The reducing behaviour of Ph₃P towards a few metal ions is however well recognized.¹

Experimental

All reagents were obtained commercially except for Me₄Si₂ which was prepared and purified as reported elsewhere.² Solvents were dried and all manipulations were carried out in a dry N₂ atmosphere.

IR spectra were recorded on a Perkin Elmer 671 spectrophotometer as KBr discs. ¹H NMR spectra (Me₄Si as internal reference) on a Varian A 50D spectrometer and ³¹P NMR spectra (85% H₃PO₄ as external reference) on a Jeol GX 400 spectrometer. Molecular weights were determined by the cryoscopic method.

Preparation of 1, 2 and 3.—Me₄Si₂ (4 mmol) in hexane (10 ml) was dropped into a solution of R₂SnCl₂ (2 mmol) in hexane (40 ml) and the mixture stirred for ca. 1 h at room temperature. The solid compound was filtered off, washed with an excess of hexane, vacuum dried and recrystallised from CH₂Cl₂/hexane [mp's: 68–70 °C (**1**), 60 °C (**2**)]. Compound **3** was prepared in the same way using Me₄Si₂ and SnCl₄ (mol ratio 2:1) in THF; it was recrystallised from CH₂Cl₂/hexane, mp 220 °C.

Reaction of 1 or 2 with Ph₃P.—To a solution of Ph₃P (2.5 mmol) in CH₂Cl₂ (30 ml) was added **1** or **2** with stirring in small portions at room temperature. The mixture was heated under reflux for ca. 8 h under a slow stream of nitrogen. The solvent was removed under reduced pressure and the solid obtained was washed with an excess of hexane, dried *in vacuo* and recrystallised from CH₂Cl₂/hexane, mp 70 °C.

Reaction of 4 with I₂.—To a solution of **4** (1 mmol) in CH₂Cl₂ (20 ml) was added iodine (1 mmol) with stirring at room temperature under a dry N₂ atmosphere. After ca. 1 h the reaction mixture was evaporated under reduced pressure and washed with hexane, giving an orange solid, mp 143 °C. The hexane washings were chromatographed on a SiO₂ column eluted with hexane, providing Ph₃P in an approximately equivalent amount (1 mmol).

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References

- S. Kozima, T. Iitani, N. Mihara, K. Sisido, and T. Ikeda, *J. Organomet. Chem.*, 1977, **44**, 117 and references cited therein.
- Z. A. Siddiqui, S. N. Qidwai, M. Jirra, and M. Shukri, *Trans. J. Met. Chem. (Weinheim, Ger.)*, 1988, **13**, 244.
- M. F. Lippert, P. P. Power, A. R. Sanger, and R. C. Sovistava, *Metal and Metallloid Amides: Synthesis, Structures, and Physical and Chemical Properties*, Harwood Wiley, Chichester, 1980.
- H. Burger and W. Siwodny, *Spectrochim. Acta, Part A*, 1970, **23**, 2841.
- A. H. Cowley, D. M. Grolando, R. A. Jones, C. M. Mann, and J. M. Power, *Polyhedron*, 1985, **7**, 1317.
- P. Foley and M. Zeldin, *Inorg. Chem.*, 1975, **14**, 2264 and references cited therein.
- H. Burger, W. Siwodny, and U. Winnig, *J. Organomet. Chem.*, 1965, **3**, 113.
- J. D. Donaldson and D. G. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1970, 145.
- H. E. Mabrouk and D. G. Luck, *J. Chem. Soc., Dalton Trans.*, 1988, 2539.
- R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1988, p. 219.
- J. C. Bailor Jr., H. J. Emelcus, R. H. Nyholm, and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Pergamon Press, New York, 1973, vol. 2, p. 58.

Coordination complexes of labile phosphorus(III) derivatives $[\text{RP}(\text{NCS})_2]$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) with first row transition metals

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$\text{RP}(\text{NCS})_2$ ($\text{R} = \text{CH}_3$ or C_6H_5) obtained from the reaction of RPCl_2 with AgSCN in CH_2Cl_2 is unstable in the absence of the solvent but affords stable solid compounds with stoichiometries $[\text{MLCl}]\text{Cl}$ ($\text{M} = \text{Mn}$ **1a**, **1b** Co **2a**, **2b** Ni **3a**, **3b** Cu **4a**, **4b**) $[\text{MLCl}]\text{Cl}_2$ ($\text{M} = \text{Fe}$ **5a**, **5b** V **6a**, **6b**) and $[\text{CuLCl}]$ **7a**, **7b** when reacted with *in situ* metal chlorides. Physico-chemical data presented here suggest that the $\text{P}(\text{NCS})_2$ moiety retains its identity in the complexes and chelates via donation at the phosphorous and sulphur atoms. The probable geometry of the complexes have been ascertained from magnetic susceptibility and reflectance spectral studies.

methylidisoithiocyanatophosphine / phenyldisoithiocyanatophosphine / transition metal complexes / synthesis and physicochemical studies

Resume – Complexes de coordination de derives labiles du phosphore (III) $\text{RP}(\text{NCS})_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) avec les metaux de transition de la premiere ligne. $\text{RP}(\text{NCS})_2$ ($\text{R} = \text{CH}_3$ ou C_6H_5) obtenus par reaction de RPCl_2 avec AgSCN dans le CH_2Cl_2 sont instables en l'absence de solvant mais donnent des composés solides stables de stœchiométrie $[\text{MLCl}]\text{Cl}$ avec ($\text{M} = \text{Mn}$ **1a**, **1b** Co **2a**, **2b** Ni **3a**, **3b** Cu **4a**, **4b**) $[\text{MLCl}]\text{Cl}_2$ ($\text{M} = \text{Fe}$ **5a**, **5b** V **6a**, **6b**) et $[\text{CuLCl}]$ **7a**, **7b** quand ils reagissent avec les chlorures metalliques *in situ*. Les données physico-chimiques suggerent que le groupe $\text{P}(\text{NCS})_2$ garde son identité dans les complexes et les chelates a travers les atomes de soufre et de phosphore. La géométrie la plus probable de ces complexes a été obtenue a partir des susceptibilités magnetiques et des spectres de réflexion.

methylidisoithiocyanatophosphine / phenyldisoithiocyanatophosphine / complexes des metaux de transition / synthèse et étude physicochimique

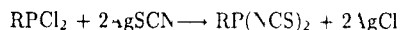
Introduction

Coordination chemistry of organic isothiocyanates have been thoroughly investigated (1). They are versatile ligands and provide different coordination sites to metal ions. Less interest has been shown however, to the derivatives where the NCS group is bonded to a non-metal atom other than carbon especially the group VA elements in the periodic table. Organophosphorous isothiocyanates $\text{RP}(\text{NCS})_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ or C_6F_5) are reported to form (2) in non-polar solvents from reaction of the appropriate halophosphine with a thiocyanating agent. However, these compounds invariably decompose if isolation from solvent is attempted. This may explain the lack of interest in the study of their reactivity towards metallic substrates. It has recently been reported (3) that stabilization of an unstable phosphoalkyne can be achieved by complex formation with metal. It is thus likely that the labile $\text{P}(\text{NCS})_2$ moiety possessing electron-rich centres can be stabilized through coordination to metals. Here we describe investigations of the reactivity of the elusive phosphorus(III) derivative $\text{RP}(\text{NCS})_2$ ($\text{R} = \text{CH}_3$ or C_6H_5) towards transition metal ions and the isolation

of stable complexes in which the $\text{P}(\text{NCS})_2$ moiety is stabilized via coordination through its P and S atoms.

Results and discussion

RPCl_2 apparently reacts with AgSCN in a metathetic exchange



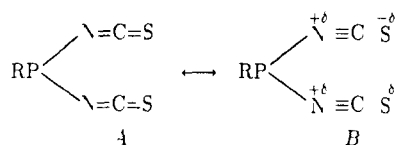
as has been ascertained from the IR spectrum of the reaction mixture. The 520 cm^{-1} band of P-Cl stretching vibration disappears with the concomitant appearance of new band at 1160 cm^{-1} assignable to $\nu(\text{P}-\text{N})$ stretching vibration (4) and with the characteristic (1, 2) ν_{asym} and ν_{sym} NCS vibrations (table I) indicative of $\text{RP}(\text{NCS})_2$. No trace of unreacted RPCl_2 was detected in the solution. The position of the characteristic NCS vibrations are identical to those found for RNCS (1) suggesting the existence of similar canonical forms (vide infra) for NCS bonding with B predominating. The IR spectrum does not show any band in the $1300-1350\text{ cm}^{-1}$ region characteristic of $\nu(\text{P}=\text{N})$ stretching vibration (4). This reveals that the phosphorus lone pair

Table I Important IR frequencies (cm^{-1}) and their assignments for $\text{RP}(\text{NCS})_2$ and the complexes

Compounds		$\text{C}_6\text{H}_5/\text{C}_6\text{H}_5$ vibrations	$\nu_{\text{asym}} \text{NCS}$	$\nu_{\text{sym}} \text{NCS}$	$\nu(\text{P}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{P})$	$\nu(\text{M}-\text{Cl})$
$\text{CH}_3\text{P}(\text{NCS})_2$	a	2960w 2920w 1390w 1235s 800m	2040s	960m	1150m			
$\text{C}_6\text{H}_5\text{P}(\text{NCS})_2$	b	1590m 1445vs 1130s 745s 715m 695vs	2020sb	970m	1160m			
$[\text{Mn}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	1a	2955w 2920w 1390w 1235s 795m	2030s	955m 920w	1150m	290m	375w	300m
$[\text{Mn}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	1b	1590m 1440vs 1120s 750m 725s 690s	2020m	990m 970w	1145m	275m	365m	300m
$[\text{Co}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	2a	2950w, 2910w 1395w 1240 810m	2060s	970m 950w	1140m	280m	390w	295m
$[\text{Co}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	2b	1590m 1450s 1130m 760m 720s 695s	2070s	980m 965w	1150m	280m	350m	300m
$[\text{Ni}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	3a	2950w 2900w 1390w 1230s 790m	2030s	970m, 950w	1140s	280m	350sh	320m
$[\text{Ni}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	3b	1590m 1440vs 1130s 760m 730vs 695vs	2040sb	980m	1150m	275m	350sh	320m
$[\text{Cu}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	4a	2970w 2930w 1390w 1235s 800m	2070s	960m 930w	1160m	295m	315w	300m
$[\text{Cu}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}$	4b	1595m 1430vs 1130s 740m 730vs 695vs	2060m	965m 945w	1150m	290m	330sh	310m
$[\text{Fe}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}_2$	5a	2960w 2910w 1380w 1240s 790m	2030m	980m	1140m	280m	320sh	300m
$[\text{Fe}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}_2$	5b	1630m 1420s 1130s 750m 725s 690s	2040m	970m	1145m	290m	325sh	310m
$[\text{V}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}_2$	6a	2950w 2900w 1390w 1240s 800s	2030m	950m	1140m	280m	350w	300m
$[\text{V}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]\text{Cl}_2$	6b	1620m 1420m 1130s 750m 725m 690s	2010m	960m 940w	1150m	290m	360sh	305m
$[\text{Cu}\{\text{CH}_3\text{P}(\text{NCS})_2\}_2\text{Cl}]$	7a	2960w 2910w 1300 1250s 810m	2070m	960mb	1150m	290m	330sh	300m
$[\text{Cu}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}_2\text{Cl}]$	7b	1590m 1440vs 1130s 750m 730vs 695vs	2080s	980m	1150m	290m	325sh	310m

vs = very strong s = strong m = medium w = weak

does not interact with the NCS bonding and the positive charge on nitrogen remains localized as in *B*



Removal of solvent has resulted in a dark reddish brown oil whose erratic analytical data do not agree with the expected stoichiometry of the product $\text{RP}(\text{NCS})_2$. The IR spectrum of the oil shows strong additional bands at 1270 and 760 cm^{-1} attributable to $\nu(\text{P}=\text{O})$ and $\nu(\text{P}=\text{S})$ stretching vibration (2) respectively. This indicates that $\text{RP}(\text{NCS})_2$ is unstable in the absence of the solvent and decomposes into the corresponding phosphoryl and/or thiophosphoryl species. We have been unable to determine the exact nature of the decomposition products. This behaviour of $\text{RP}(\text{NCS})_2$ is in contrast to that of the corresponding $(\text{RO})\text{P}(\text{NCS})_2$ which is known to be fairly stable under normal conditions (5). This may reasonably be accounted for an additional $p\pi-d\pi$ overlap between the filled non-bonding $p\pi$ orbital of oxygen and the empty low lying $d\pi$ orbital of phosphorus. This additional $(\text{P}-\text{OR})\pi$ bond overlap in phosphorus (V) derivatives is known to influence

their reactivity (6) towards nucleophiles. The absence of similar π overlap in $\text{RP}(\text{NCS})_2$ may have a labilizing effect. However, the unstable $\text{RP}(\text{NCS})_2$ has shown reactivity towards transition metal ions giving stable solid compounds.

The stoichiometry of the compounds verified from analytical results are shown in table II. These are monomeric, behaving as 1:1 electrolytes except for 7a, 7b (non electrolytes) and 5a, 5b, 6a, 6b (1:2 electrolyte) in DMSO (7). The important bands observed in the IR spectra of the compounds are in table I. The positions of the characteristics NCS frequencies do not differ significantly after complexation from that in free ligand, hence indicating that structure *B* predominates in the complexes also and that the sulphur rather than the nitrogen atom of the NCS group coordinates. The lone pair at nitrogen is partially used in bonding within the NCS group. The $\text{M}-\text{S}$ bond in the complexes is probably further stabilized (8) by additional back donation from the metal ion to sulphur. The characteristic $\nu(\text{M}-\text{S})$, $\nu(\text{M}-\text{P})$ and $\nu(\text{M}-\text{Cl})$ bond frequencies were observed at the appropriate positions (9, 10) in the far IR region. As the lone pair at phosphorus is free and does not interact with the NCS bonding (vide supra), owing to its directional nature (sp^3 hybrid) coordination through phosphorous would not affect the characteristic $\text{P}-\text{N}$ bond frequency. It can therefore be

Table II. Physical data of the $\text{RP}(\text{NCS})_2$ complexes.

Complexes		m-pt (°C)	Colour	Found (Calculated)%					$\Delta M(\text{Ohm}^{-1}\text{cm}^2\text{Mol}^{-1})$
				C	H	N	Cl	M	
$[\text{Mn}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	1a	150	light yellow	12.62 (12.51)	1.02 (1.04)	9.52 (9.73)	23.98 (24.63)	19.91 (19.09)	67
$[\text{Mn}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	1b	175	-do-	27.44 (27.44)	1.40 (1.40)	8.3 (8.0)	20.84 (20.27)	16.20 (15.68)	71
$[\text{Co}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	2a	260	greenish yellow	12.41 (12.34)	1.06 (1.03)	9.35 (9.60)	24.95 (24.30)	20.85 (20.20)	56
$[\text{Co}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	2b	310	-do-	27.13 (27.11)	1.43 (1.40)	7.6 (7.6)	20.2 (20.0)	16.4 (16.6)	54
$[\text{Ni}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	3a	235	yellow	12.27 (12.35)	1.02 (1.03)	9.58 (9.60)	24.15 (24.32)	20.36 (20.13)	60
$[\text{Ni}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	3b	280	-do-	21.16 (21.14)	1.40 (1.42)	7.90 (7.90)	20.12 (20.00)	16.18 (16.00)	67
$[\text{Cu}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	4a	147	chocolate	12.18 (12.14)	1.06 (1.01)	9.42 (9.44)	23.75 (23.92)	21.52 (21.43)	53
$[\text{Cu}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}$	4b	280	-do-	27.05 (27.00)	1.42 (1.40)	7.84 (7.82)	19.76 (19.78)	17.92 (17.7)	55
$[\text{Fe}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}_2$	5a	140	orange	11.07 (11.10)	0.91 (0.93)	8.58 (8.64)	32.78 (32.81)	17.12 (17.23)	118
$[\text{Fe}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}_2$	5b	165	-do	24.80 (24.85)	1.34 (1.30)	7.0 (7.20)	27.50 (27.54)	14.40 (14.44)	121
$[\text{V}\{\text{CH}_3\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}_2$	6a	160	greenish yellow	11.31 (11.28)	1.02 (0.94)	8.81 (8.77)	33.81 (33.31)	16.22 (15.95)	116
$[\text{V}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}\text{Cl}]\text{Cl}_2$	6b	195	-do-	25.15 (25.17)	1.30 (1.32)	7.35 (7.35)	27.93 (27.90)	13.51 (13.34)	115
$[\text{Cu}\{\text{CH}_3\text{P}(\text{NCS})_2\}]\text{Cl}$	7a	202	off-white	13.81 (13.79)	1.16 (1.15)	10.72 (10.73)	13.67 (13.58)	24.95 (24.35)	20
$[\text{Cu}\{\text{C}_6\text{H}_5\text{P}(\text{NCS})_2\}]\text{Cl}$	7b	230	-do-	29.74 (29.72)	1.49 (1.50)	8.40 (8.60)	11.21 (10.98)	20.05 (19.65)	15

emphasized that, like the unstable phospho-alkyne (3) the labile $\text{RP}(\text{NCS})_2$ too is stabilized via complex formation with metal and $-\text{P}(\text{NCS})_2$ moiety is retained in the complexes.

The ^{31}P MNR spectra of the complexes recorded in $d^6\text{DMSO}$ showed a single resonance between +18 to +45 ppm region (H_3PO_4 external reference). The signal lies considerably, up-field compared to that (2) in the uncomplexed moiety, but is in the range reported for transition metal phosphine complexes (11). Thus chelation to metal is accompanied by a large increase in phosphorous shielding, probably due to additional overlap between the empty $\text{P}(3d\pi)$ and metal $(3d\pi)$ orbitals effecting the delocalization of metal electrons. The observed broadening (excepting 3 and 7) of the signal is due to the presence of paramagnetic species in solution.

The reflectance spectra of 1a, 1b and 5a, 5b were nearly identical in nature containing weak bands in the visible (ligand field) region. The weak intensity of the bands is due to the forbidden nature of the originating transitions (12); assignments of the observed transitions arising from the ^6S ground state to the quartet excited states derived from the ^4G and ^4D levels are indicated in table III. The μ_{eff} value of 1a, 1b is consistent with the d^5 configuration (13) of the metal ion. However, for 5a, 5b the μ_{eff} value is lower than the expected spin only value, which may reasonably be due to antiferromagnetic behaviour, occurring in some of the iron complexes (18). The μ_{eff} value of 2a, 2b

(table III) indicates a high spin d^7 configuration of the cobalt ion in the complex. The position of the bands observed in the reflectance spectrum are characteristic of a tetrahedral environment around the ion. The reflectance spectrum of 3a, 3b is characteristic of square-planar nickel(II) (12) which is further confirmed from the observed diamagnetic nature of the complex. A single broad band observed in the ligand field region of 4a, 4b can be assigned to the $d-d$ transition characteristic of pseudo tetrahedral environment around copper(II) ion. For regular tetrahedral copper(II) complexes the region 10,000-20,000 cm^{-1} is reported (12) to be blank. The absence of a band in the 14000-16000 cm^{-1} region, however, rules out any possibility of square-planar geometry (12) for the complex. The μ_{eff} value is consistent with the d^9 configuration of the copper ion. These observations indicate that 4a, 4b is a genuine copper(II) complex which seems to constitute unusual behaviour for $\text{RP}(\text{NCS})_2$, compared with that known for reactions (14) of Ph_3P or substituted halophosphines with $\text{Cu}(\text{II})$ salts, which invariably result in a redox process with generation of copper(I) species. The magnetic moment and observed bands in the reflectance spectrum of 6a, 6b are indicative of a tetrahedral configuration (12, 13) of the complex. The expected diamagnetic nature of 7a, 7b and absence of any ligand field bands are due to a d^{10} configuration of the metal ion. However, tetrahedral geometry may reasonably be proposed from the observed stoichiometry, non-electrolyte nature of the solutions and IR spectral information.

[illegible]

- (1) Villa JF *Inorg Chim Acta* (1979) **32**, 199 and references therein
- (2) Sowerby DB *J Inorg Nucl Chem* (1961) **22**, 205; Oba K, Watari F, Aida K *Spectrochim Acta* (1967) **23A**, 1545; Ali R, Dillon KB *Polyhedron* (1986) **5**, 1197

- (3) Burkett JCTR Sr, Hitchcock LPB, Kroto HW, Nixon JF *J Chem Soc Chem Commun* (1981) 1141
- (4) Nickle E, Gudat G, Symella E *Angew Chem Int Ed Engl* (1986) **25**, 834
- (5) Duff E, Iripett S, Whittle PJ *J Chem Soc Perkin I* (1973) 972
- (6) Edwards JO *Inorganic Reaction Mechanism* W Benjamin New York (1965) p 57
- (7) Smith HD Jr, Robinson MA, Papetti S *Inorg Chem* (1967) **6**, 1014
- (8) Turco A, Peate C *Nature* (1961) **191**, 66
- (9) Sabatini A, Bertini I *Inorg Chem* (1965) **4**, 350
- (10) Clark RJH, Williams S *Inorg Chem* (1965) **4**, 959
Siddiqi ZA, Qidwai SN, Jaria M, Shakir M *Transition Met Chem* (1988) **13**, 244-317
- (11) Crabtree RH *The Organometallic Chemistry of the Transition Metals* John Wiley New York (1988) p 219
- (12) Lever ABP *Inorganic Electronic Spectroscopy* Elsevier, Amsterdam 1984
- (13) Figgis BN, Lewis J *Prog Inorg Chem* (1964) **6**, 37
- (14) Mc Auliff CA, Levason W *Phosphine, Arsine and Stibine Complexes of the Transition Elements* Vol I Elsevier, Amsterdam 1979
- (15) Reilly CN, Schmid RW, Sadak FA *J Chem Educ* (1959) **36**, 619